The Preparation of Functionalized Polymers by Ring-Opening Metathesis Polymerization

Thesis by

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To Mom and Dad

I feel very fortunate to have worked under the direction of Bob Grubbs for the past five years. During my time at Caltech Bob gave me room to improvise and was always there when I needed help. His enthusiasm for science and his equable temperament were constants that made working for and with him a very pleasurable experience. I am very grateful for all I have learned from Bob, and I hope to learn more from him in the ensuing years. Bob, thank you for everything.

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ABSTRACT

The preparation of polymers that contain functional groups either along the backbone, as side chains, or at the chain ends by ring-opening metathesis polymerization (ROMP) was investigated.

In Chapter 1, the recently developed aqueous ROMP was exploited in the synthesis of a polymer with pendant imide groups. The polymerization of *exo-N*-methyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide was accomplished in aqueous solution under mild conditions using the simple ruthenium(II) coordination complex $Ru^{II}(H_2O)_6tos_2$ (tos=*p*-toluenesulfonate). The resultant high molecular weight polymer was isolated in high yield, exhibited a T_g of 225 °C, and was thermally stable up to 402 °C. Hydrogenation of the polymer yielded its saturated analog which exhibited a lower T_g (170 °C) but a higher temperature of decomposition (430 °C). Requirements for successful polymerization were investigated.

In Chapter 2, the ROMP of a variety of 5-substituted cyclooctenes by the well-defined metathesis catalyst $(PCy_3)_2(Cl)_2RuCHCHCPh_2$ (**1**) was accomplished. The polymers were obtained in moderate to good yields. The structures of the polymers were investigated by IR, ^1H NMR, and ^{13}C NMR spectroscopies. The molecular weight of one of the derivatives was controlled by varying the monomer to catalyst ratio and by the addition of a chain transfer agent to the polymerization solution. The thermal properties of the polymers are reported.

In Chapter 3, the ring-opening metathesis polymerization (ROMP) of cyclooctadiene (**COD**) by three well-defined metathesis catalysts in the presence of a variety of chain transfer agents (CTAs) is described. Expressions for the

theoretical molecular weight and functionality were derived for this type of ROMP system. Hydroxytelechelic polybutadienes (HTPBDs) synthesized contained one type of regiochemistry in the repeat unit (1,4) and one type of alcoholic endgroup. The molecular weight of the HTPBDs was controlled by the ratio of COD to CTA and number average functionalities that approached 2.0 were obtained at high CTA to catalyst ratios.

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Chapter 1

Aqueous Ring-Opening Metathesis Polymerization of Carboximide-Functionalized 7-Oxanorbornenes[1]

Abstract: The ring-opening metathesis polymerization (ROMP) of *exo-N*-methyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (**1**) was accomplished in aqueous solution under mild conditions using the simple ruthenium(II) coordination complex $Ru^{II}(H_2O)_6tos_2$ (tos=*p*-toluenesulfonate) (**2**). The polymerization yield was nearly quantitative. The resultant high molecular weight polymer (poly-**1**) exhibited a T_g of 225 °C and was thermally stable up to 402 °C. The thermal and radiative stabilities of poly-**1** were further investigated. Poly-**1** was hydrogenated to yield its saturated analog, which had a lower T_g (170 °C) but a higher temperature of decomposition (430 °C). Complex **2** was deactivated by coordination of free maleimides formed during the polymerization of carboximide-functionalized monomers capable of undergoing retro Diels-Alder chemistry. The scope of this polymerization was therefore limited to carboximide-functionalized monomers that are stable toward retro Diels-Alder reactions at the polymerization temperature. Both ruthenium(II)-**1** and ruthenium(II)-*N*-methylmaleimide olefin complexes were identified.

Introduction

The design and synthesis of functionalized polymers, polymers whose properties depend to a significant extent on the functional group substituents along the backbone of the macromolecule, is an active area of research.[2-4] The synthesis of these polymers through the polymerization of functionalized monomers is ideal, as it enables the direct incorporation of functionality into the polymer backbone and thus circumvents the potential difficulty of chemical transformations on a polymeric substrate.[2] An increased variety and availability of functionalized polymers requires the further development of polymerizations that are compatible with functionality in a monomer. In the case of the ring-opening metathesis polymerization (ROMP),[5-8] initial efforts in the search for a catalyst system effective for the polymerization of functionalized substrates were met with limited success.[6,9,10] One overwhelming problem with most of the early transition metal ROMP catalysts is the high reactivity of the catalysts toward polar functionality present in the monomer. As a result, poisoning of the catalyst and polymerization become competitive processes. At the present time, the industrially useful polymers prepared via ROMP contain only olefinic functionality (Figure 1).[11]

Recent advances in the preparation of functionalized polymers via ROMP include the polymerization of functionalized norbornenes and 7-oxanorbornenes employing well-defined molybdenum based catalysts.[12-15] Late transition-metal metathesis catalysts have been shown to be more tolerant of polar substrates than their early transition metal counterparts.[6] For example, the emulsion polymerization of norbornene and its derivatives by

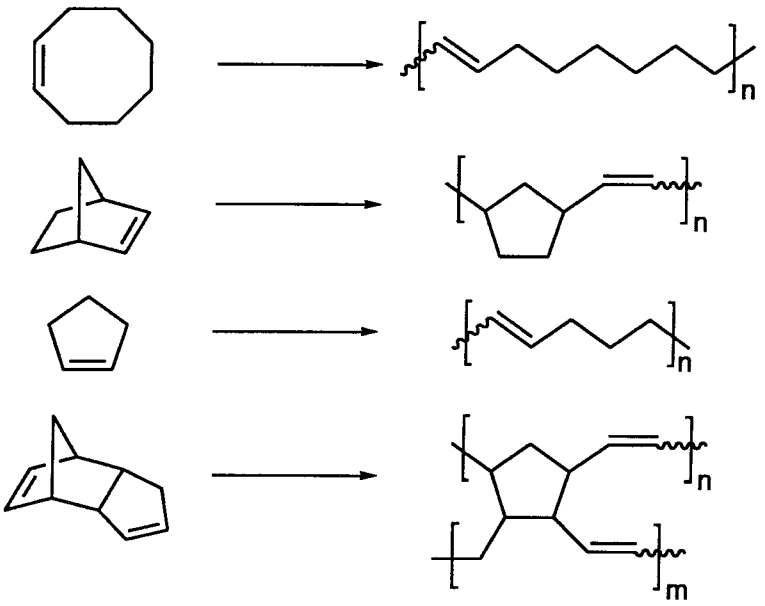


Figure 1. Industrially useful polymers prepared via ROMP.

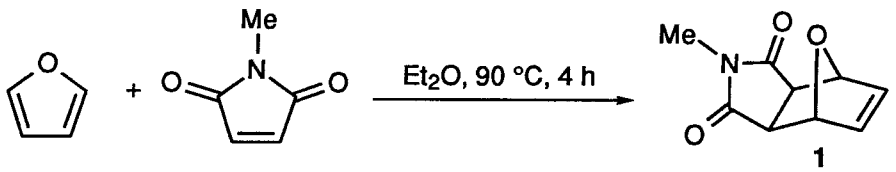
ruthenium, iridium, and osmium complexes in *aqueous ethanol* was reported over 20 years ago.[16,17] The polymerization of functionalized monomers with these catalysts was possible but not very efficient.[18] Recently, we reported that simple ruthenium(II) complexes effected the polymerization of functionalized 7-oxanorbornenes *under air in an entirely aqueous environment*.[19] Water was shown to have the beneficial effect of decreasing the initiation time of the polymerization relative to the polymerization in organic solvents.[19-21] The simple ruthenium coordination complex $Ru^{II}(H_2O)_6(tos)_2$ (tos=*p*-toluenesulfonate) (**2**) was found to be the most active catalyst employed, giving high molecular weight, low-dispersity materials in almost quantitative yields. In addition, **2** was recyclable for a minimum of 14 consecutive polymerizations and was active for the polymerization of a variety of 7-oxanorbornene derivatives including hydroxyl, carboxyl, and

alkoxy substituted monomers.[19,20] Feast and Harrison have also successfully polymerized 7-oxanorbornenes in water using ruthenium, iridium, and osmium chlorides as catalysts.[22,23] The enhanced tolerance of the late transition metal coordination catalysts towards polar solvents, polar functional groups, and air facilitated the following investigation of the polymerization of carboximide-functionalized 7-oxanorbornenes.

Results and Discussion

The ROMP of carboximide-functionalized norbornenes has been independently investigated, and the polymers obtained possessed high T_g values, high thermal resistances, and good mechanical properties.[24,25] In one case, however, only a 7% yield was reported for the polymer obtained from the polymerization of the Diels-Alder adduct of cyclopentadiene and *N*-propylmaleimide employing a classical tungsten-based metathesis catalyst.[24] More recently, Asrar has described the synthesis and ROMP of a number of carboximide-functionalized norbornenes employing a classical tungsten-based catalyst system.[26,27] High T_g, thermally robust polymers were obtained, and the yields of the polymerizations were much higher than obtained in earlier systems. The desirable properties of these carboximide-functionalized ROMP polymers in combination with the efficiency, mildness, and robust characteristics of the aqueous system mentioned above prompted this investigation of the polymerization of carboximide-functionalized 7-oxanorbornenes.

Monomer Preparation. The Diels-Alder adduct of furan and *N*-methylmaleimide, *exo*-*N*-methyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (**1**), was prepared by combining furan and *N*-methylmaleimide in diethyl ether, degassing the reaction mixture, and heating to 90 °C for four hours in a heavy-walled glass tube (eq 1).

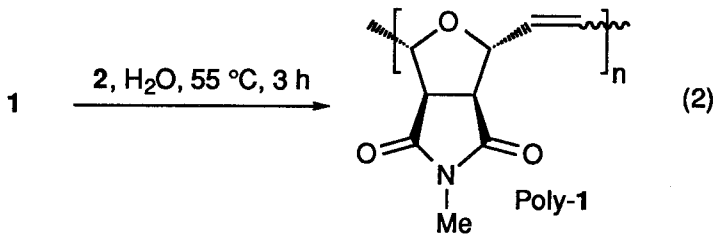


(1)

1

Compound **1** crystallized from the reaction upon cooling and was isolated in 95% yield. The reaction was conducted on a multigram scale, and the white crystalline material was stored at room temperature, under air, for several months with no detectable decomposition. Monomer **1** can be recrystallized from water or ethyl acetate.[28] However, the as-synthesized material was of high purity as determined by ^1H NMR spectroscopy and was polymerized without further purification. The adduct formed is entirely the exo isomer, as determined by ^1H and ^{13}C NMR spectroscopy.[29,30] The endo isomer can be synthesized at lower temperatures and subsequently isomerized to the exo isomer by heating to 90 °C in the presence of excess furan.

Polymerization Procedure. The polymerization of **1** was conducted in pure water or water/ethanol solutions at 55-60 °C employing $Ru^{II}(H_2O)_6tos_2$[31,32] (**2**) as the catalyst (eq 2).



(2)

Complex **2** was the most active catalyst for this polymerization and was used throughout the study ($RuCl_3$ and K_2RuCl_5 were also effective catalysts for the polymerization of **1** but had longer initiation times). The general polymerization procedure consisted of adding either degassed ethanol/water (1:1 v/v) or pure water to a mixture of **1** and **2** under argon (typically, [monomer]≈0.4 M and [Ru]≈0.003 M, [**1**]/[**2**]=133). The reaction was heated to 55-60 °C in an oil bath for three hours. As the monomer dissolved, the

polymerization solution turned yellow, consistent with the formation of a ruthenium-olefin complex.[19,33] Within 5-15 minutes polymer (poly-**1**) particles began to precipitate from the solution, and immediately thereafter the reaction flask became filled with polymer. After three hours the polymer was filtered, washed successively with water and acetone, and dried. The crude yield of the off-white polymer was between 85 and 98% in all cases.[34]

The polymerization can be achieved under air without any degassing of the solvents,[35] however, there was a marked effect of oxygen on the molecular weight of the resultant polymer. When the polymerization was run under rigorously oxygen-free conditions, the polymer formed had a molecular weight average triple that of the polymer obtained from a non-degassed solution. When water that had been sparged with oxygen was used in the polymerization, no poly-**1** was formed, and the resulting polymerization solution became dark green. This color is presumably due to oxidation of the ruthenium to a species that is inactive for polymerization. Although the exact role that oxygen plays in the polymerization mechanism is not fully understood,[36] this supports the claim that ruthenium(II) is the necessary oxidation state for catalyst initiation.[19,20]

Polymer Characterization. Poly-**1** was purified by dissolution in methylene chloride and precipitation from methanol. Poly-**1** is a white, flocculent solid that is soluble in methylene chloride, chloroform, DMF, and DMSO and can be cast into tough films from these solutions. It was stable for months under air at room temperature as evidenced by no change in its molecular weight, solubility, polydispersity index (PDI), and ^{1}H NMR spectrum. In contrast, polynorbornenes and other polyalkeneamers undergo radical-induced crosslinking reactions under air in the absence of a

stabilizer.[37] The ^1H and ^{13}C NMR spectra of poly-**1** were consistent with the unsaturated polymer backbone of ROMP polymers. The ^1H NMR spectrum is shown in Figure 2. Both cis and trans resonances are observed for the olefinic protons and the allylic protons. The backbone double bonds are predominantly trans (80%), as determined by integration of the olefinic region of the ^1H NMR spectrum of poly-**1**, and initial investigations show that the polymer is essentially atactic (see below). The IR spectrum of poly-**1** shows characteristic absorbances for the imide carbonyl stretch (1779 cm^{-1}) as well as the trans olefinic out-of-plane C-H bend (970 cm^{-1}). All of the polymer samples synthesized were of high molecular weight. The $\overline{Mw}$ of the polymer samples, as determined by gel permeation chromatography (GPC) using polystyrene standards, ranged from 200K to 1100K, and the PDI ranged from 1.7 to 4.5.[38]

The thermal properties of poly-**1** are of interest since it has been reported that the norbornene analogs of poly-**1** exhibit high T_g values.[24-27] Initial differential scanning calorimetry (DSC) results showed that poly-**1** undergoes an irreversible exothermic reaction between 230 and 260 °C under argon, and no T_g or melting point was observed before the onset of the exotherm or during repeated scans. In a melting point apparatus, an abrupt change in the color of poly-**1** from white to yellow was observed between 245 and 255 °C, and the yellow polymer was no longer soluble in the solvents previously mentioned. The exothermic transition between 230 and 260 °C, the insolubility of the resultant polymer, and the change in color were presumably due to a thermally induced crosslinking reaction. However, when poly-**1** was rigorously purified (by dissolution in methylene chloride and precipitation in methanol three times), dried under dynamic vacuum

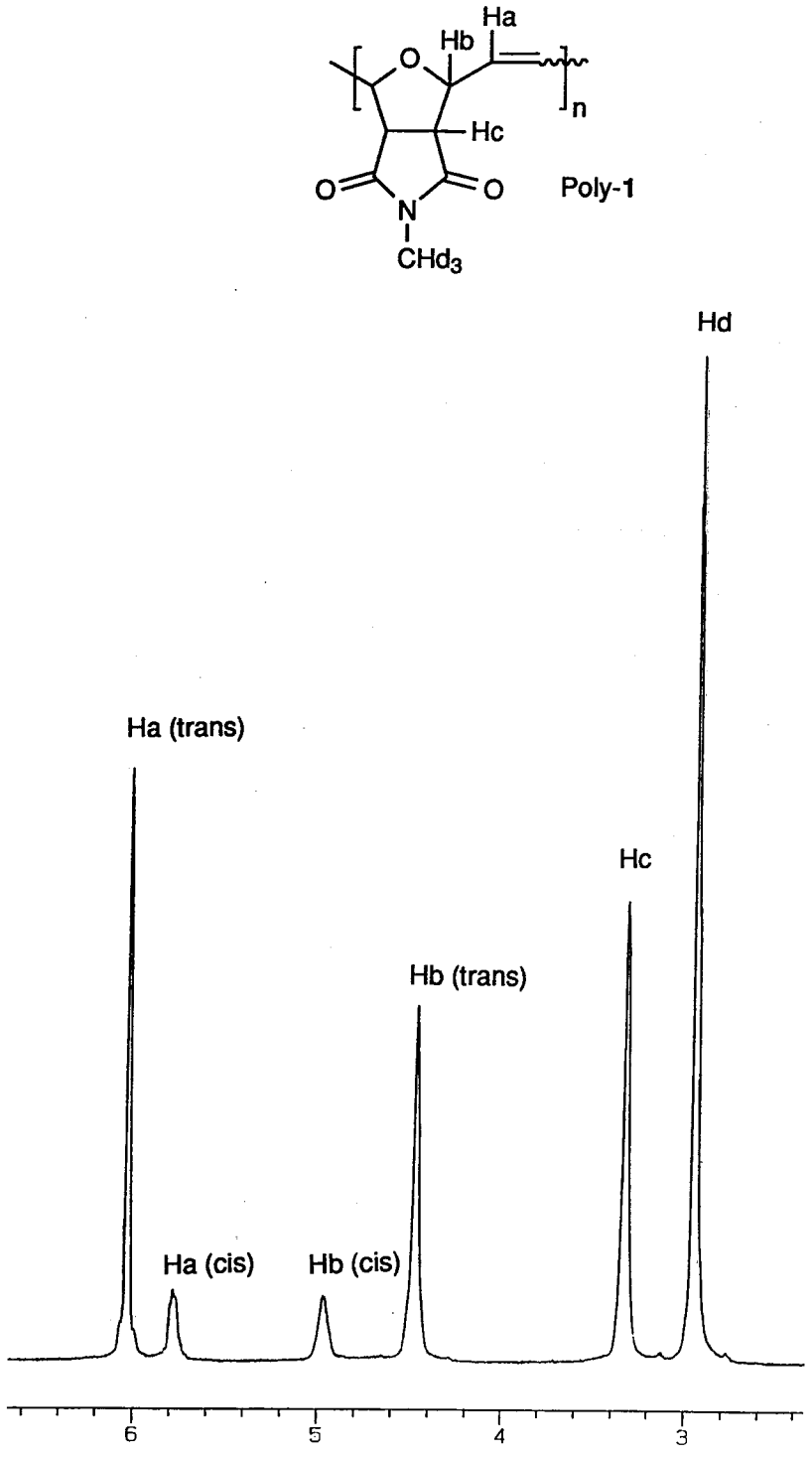


Figure 2. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of poly-**1** (scale is in ppm).

overnight and then heated to 230 °C at a scanning rate of 20 °C/minute, a T_g was observed at 225 °C. The T_g was seen upon cooling the sample and reheating, but the heat capacity per gram of polymer decreased with every cycle, the characteristic "step" became broader, and the inflection point moved to higher temperatures. Thermal mechanical analysis of a thin film of poly-**1** shows a softening temperature around 210 °C and corroborated the value for the T_g as determined by DSC. These results indicate that poly-**1** has a high T_g (225 °C), but at temperatures close to the T_g the polymer undergoes a degradative process believed to be crosslinking of the polymer backbone. The temperature at which this crosslinking reaction occurred was dependent on the purity of the sample tested. Trace amounts of ruthenium may have catalyzed decomposition of the polymer sample prior to or around the glass transition temperature.

As described previously, poly-**1** was stable under air for months at room temperature. The temperature at the onset of substantial mass loss (T_d) for poly-**1** under an argon atmosphere was determined by thermogravimetric analysis (TGA) to be 402 °C (Figure 3). The T_d dropped to 373 °C under an atmosphere of air. Isothermal aging of the poly-**1** was also performed, and the percent weight loss over a four-hour period was determined at three temperatures under both argon and air. These results are shown in Table 1. Poly-**1** underwent substantial weight loss under air at both 300 and 350 °C, but under argon at 250 °C and 300 °C the polymer lost less than one percent of its mass. This observation is in accordance with the supposition that the polymer undergoes crosslinking at 250 °C and 300 °C under argon, but decomposition with concomitant loss of small molecules is not occurring at these temperatures.

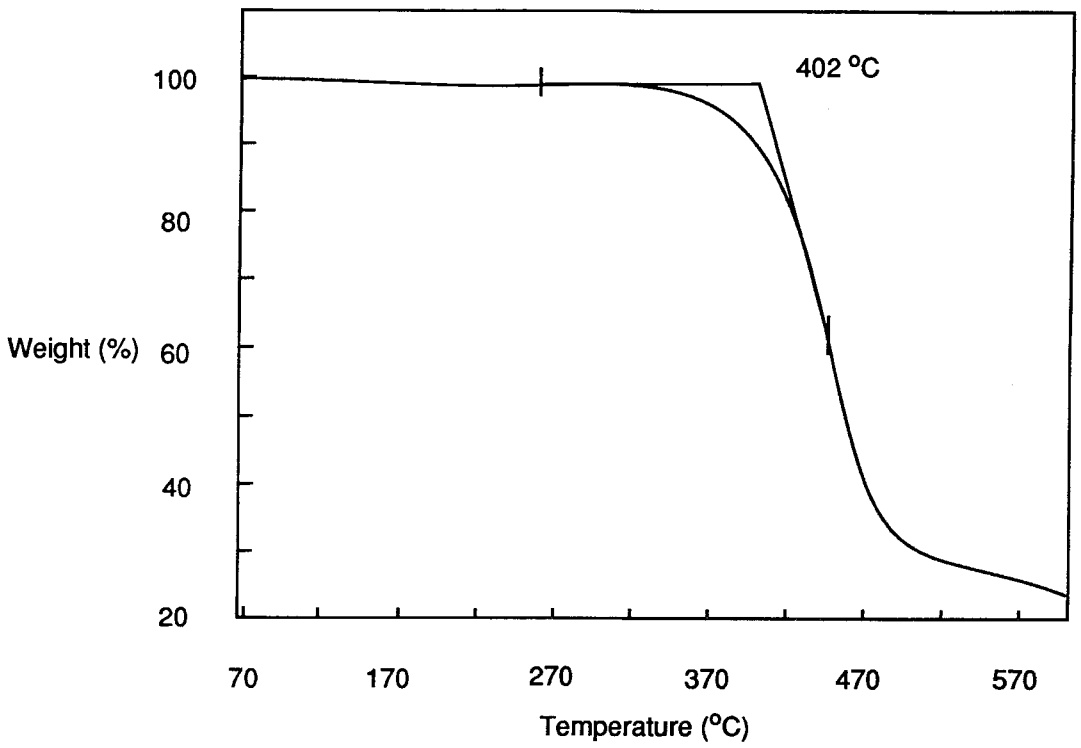


Figure 3. Thermogravimetric analysis of poly-**1** under argon.

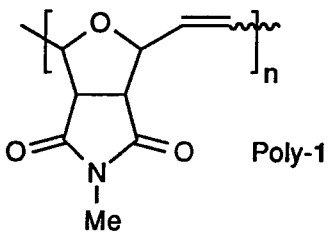
Table 1. Isothermal Aging of Poly-1

sample	temperature (°C)	atmosphere	% weight[a]
1	250	argon	99
2	300	argon	99
3	350	argon	92
4	250	air	97
5	300	air	90
6	350	air	78

[a] Percent of the weight remaining after 4 h

The susceptibility of poly-**1** to crosslinking reactions upon exposure to ultraviolet (UV) radiation was also investigated. Since poly-**1** could easily be cast into a film, examination of the change in the infrared (IR) spectrum of the polymer over time upon exposure to UV radiation was an effective means of investigating crosslinking in the polymer sample. The polymer was cast into a thin film and mounted in an IR cell. The IR spectrum of the polymer film was taken, and the film was then mounted in a photolysis box and subjected to a UV lamp. The IR spectrum showed a general broadening of absorbances over time. The trans olefinic out-of-plane C-H bend at 970 cm^{-1} diminished, and the aliphatic C-H bending region became broader and more intense. This region is shown in Figure 4. After 18.5 hours the polymer film changed from colorless to dull yellow and became extremely brittle and insoluble. These results suggest that crosslinking occurred upon exposure to UV light, and the polymer lost its structural integrity. A thin film of poly-**1** exposed to sunlight for a few weeks also became slightly yellow and tore much more easily than a film stored in the dark.

Polymer Hydrogenation. Hydrogenation of polymers that contain sites of unsaturation along the backbone is a useful method for generating new products and for increasing the oxidative and thermal stability of polymers.[39-41] The hydrogenation of poly-**1** was explored using both catalytic and stoichiometric hydrogenation methods. Limited success was obtained using diimide (generated from the decomposition of *p*-toluenesulfonhydrazide at 110 °C in DMF) as a stoichiometric hydrogenation method. The resultant product was sparingly soluble or insoluble and therefore difficult to characterize. Catalytic hydrogenation of poly-**1** was more successful. Partial hydrogenation was accomplished at room temperature using Wilkinson's



Poly-1

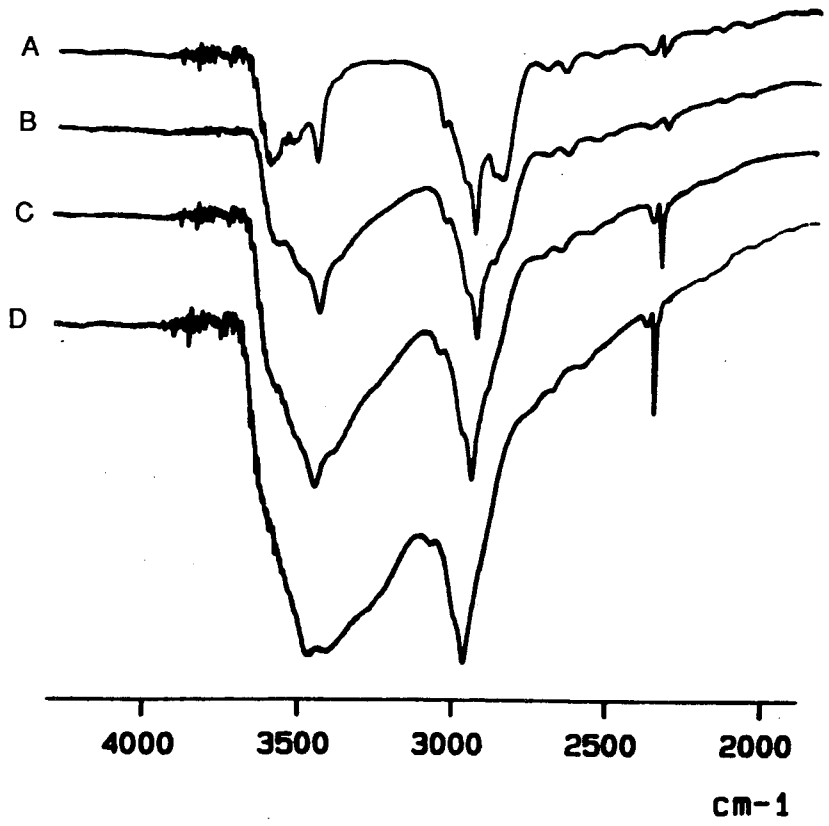
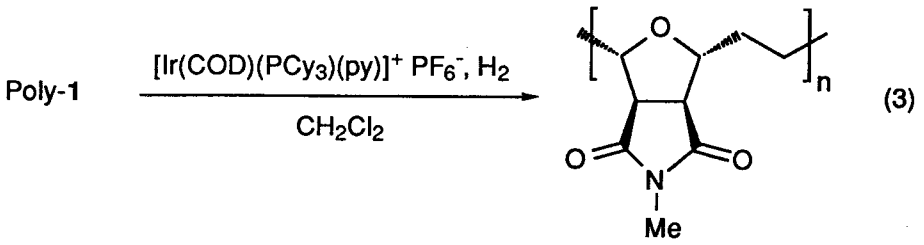


Figure 4. IR spectra of a poly-1 film exposed to UV radiation. A = initial, B = 1 h, C = 4 h, D = 18.5 h.

catalyst $[RhCl(PPh_3)_3]$[42] under a flow of hydrogen. Complete hydrogenation, as determined by lack of olefinic resonances in the ^1H NMR spectrum, of poly-**1** was achieved using Crabtree's catalyst $[Ir(COD)(PCy_3)(py)]^+PF_6^-$[43] at room temperature under a hydrogen atmosphere (eq 3).



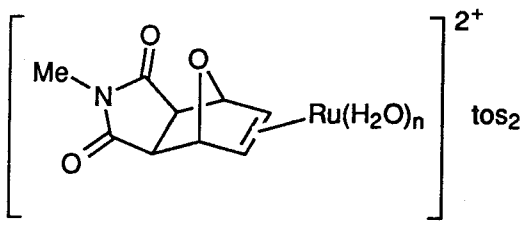
(3)

A double bond to catalyst concentration ratio of less than 100 was necessary for complete hydrogenation (ratios greater than this result in only partial hydrogenation).

Hydrogenated poly-**1** was a white solid that could be cast into tough films that were more flexible than their unsaturated counterparts. The totally hydrogenated samples had GPC chromatographs similar to those obtained for the unsaturated analogs. Hydrogenated poly-**1** had a T_g of 170 °C and a T_d of 430 °C, and all of the partially hydrogenated samples had lower T_g's and higher T_d's than poly-**1**. The decrease in the T_g was interpreted as an increase in the flexibility of the polymer backbone upon hydrogenation. The increase in the T_d of hydrogenated poly-**1** suggests that the initial decomposition process in poly-**1** involved chemistry at the carbon-carbon double bond. Unlike the DSC trace of poly-**1**, the DSC trace of hydrogenated poly-**1** showed no thermal transition other than a T_g below 350 °C, and the polymer did not change in color upon heating to 300 °C. Analysis of the ^{13}C NMR spectrum of hydrogenated poly-**1** indicated that the polymer is essentially atactic. This

observation was not surprising since the lability of water ligated to the ruthenium(II) metal center offers more than one site for the incoming olefin to react with the propagating carbene. Thus, the polymerization becomes random with respect to stereoregularity along the polymer backbone. Similar results have been obtained for the polymerization of other 7-oxanorbornenes employing **2** as the catalyst.[44]

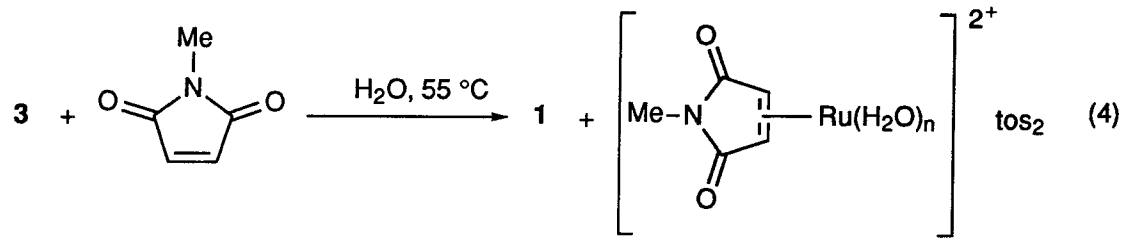
Polymerization Catalysis. In the aqueous polymerizations we reported earlier,[19] a ruthenium-monomer olefin complex was observed by NMR spectroscopy in the polymerization solution. These monomer complexes were reported to be highly active catalysts for subsequent polymerizations and were shown to be recyclable. In the present case of the aqueous polymerization of **1**, a ruthenium-**1** complex (**3**) was also characterized in the polymerization solution.



3

Approximately 70% of the initial $Ru^{II}(H_2O)_6tos_2$ was converted to **3** as determined by ^1H NMR spectroscopy. Solutions containing **3** proved to be active polymerization catalysts and can be recycled for the catalysis of subsequent polymerizations. Olefin complexes of this type were prepared for other derivatives of **1**, including *exo-N*-phenyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (**4**) and the endo isomer of **1**. However, neither the endo isomer of **1** nor **4** polymerizes under the conditions described above. It was

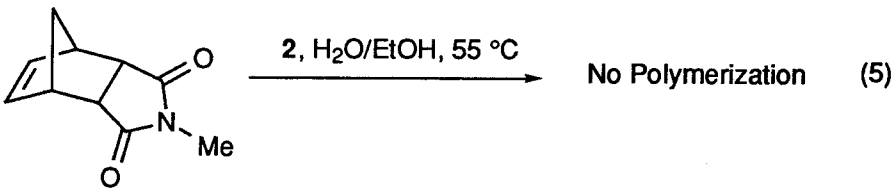
discovered that both of these compounds undergo an endo-exo isomerization at the polymerization temperature. This isomerization results in the formation of free maleimides in solution. Maleimides are excellent π acceptors[45] capable of forming strong olefin complexes with the ruthenium(II) metal center. Consequently, in the attempted polymerization of the endo isomer of **1** a 1:1 ruthenium(II)-*N*-methylmaleimide complex formed, and no polymer was isolated. The analogous *N*-phenylmaleimide complex was also observed during the unsuccessful polymerization of **4**. The lack of reactivity of endo-**1** and **4** was attributed to the facile retro Diels-Alder chemistry at the polymerization temperature. The role of maleimides as catalyst poisons was further substantiated by the failure of **1** to polymerize in the presence of *N*-methylmaleimide. The polymerization solution did become yellow, suggestive of an olefin complex formation. This species was identified as a 1:1 ruthenium(II)-*N*-methylmaleimide complex by ^{1}H NMR spectroscopy and cyclic voltametry. Also, in an NMR experiment it was observed that *N*-methylmaleimide quantitatively displaced **1** from the olefin complex **3** at 55 °C (eq 4).



(4)

If a ruthenium-**1** olefin complex is on the pathway to an initiating species for the polymerization, the presence of maleimides effectively eliminates catalyst activation.

The endo isomer of **1** was the kinetic product of the Diels-Alder reaction of furan and *N*-methylmaleimide, and the isomerization to the more stable exo isomer occurred at the polymerization temperature. The kinetic product in the Diels-Alder addition of cyclopentadiene and *N*-methylmaleimide (**5**) was also the endo isomer. Although compound **5** was stable towards retro Diels-Alder chemistry at the polymerization temperature of 55-60 °C, it did not polymerize under the typical polymerization conditions (eq 5).



The inertness of endo isomers toward ROMP employing late transition-metal catalysts has previously been reported.[6,7] Two explanations for this lack of reactivity have been suggested: (1) chelation of the catalyst by the olefin and the endo functionality and (2) the steric restrictions due to transannular crowding of the four cis substituents on the five-membered ring in the repeat unit. In the case of the endo isomer of **1**, however, the lack of reactivity may also be attributed to the poisoning of the catalyst by *N*-methylmaleimide.

Conclusions

The scope of the aqueous ruthenium polymerization system was expanded to include the polymerization of carboximide-functionalized 7-oxanorbornenes. In the case of **1**, the polymerization was accomplished under mild conditions using a simple ruthenium(II) catalyst to yield high molecular weight polymer in near quantitative yields. The resultant polymer possessed a high degree of thermal and oxidative stability as well as a high glass transition temperature. Catalytic hydrogenation of poly-**1** yielded its saturated analog, which had a higher decomposition temperature and a lower glass transition temperature than the parent polymer. Furthermore, it was determined that a requirement for the successful polymerization of carboximide-functionalized substrates is that they be stable toward retro Diels-Alder chemistry, since the presence of maleimides in the polymerization solution poisons the catalyst by forming a stable maleimide complex. Further studies of the chemistry of this type of ruthenium-olefin complex[33] and the extension of this polymerization system to the preparation of other functionalized polymers is currently being investigated in our group.

Experimental Section

General Considerations. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4Å molecular sieves (Linde). NMR spectra were recorded on a JEOL GX-400 spectrometer (399.65 MHz ^{1}H, 100.40 MHz ^{13}C). All chemical shift values are given in ppm and are referenced with respect to residual protons in the solvent. IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. Gel permeation chromatographs were obtained on a HPLC system utilizing an Altex Model 110A pump, a Rheodyne model 7125 injector with a 100 μL injection loop, through either three Shodex Styragel columns (KF 803, KF 804, and KF 805) or an American Polymer Standards 10 micron mixed bed column, and a Knauer differential-refractometer. Methylene chloride was used as the eluent at a flow rate of 1.0 mL/min. The molecular weights and polydispersities are reported versus monodisperse polystyrene standards. Elemental analysis was performed by Fenton Harvey at the California Institute of Technology Elemental Analysis Facility. Differential scanning calorimetry was performed on a Perkin-Elmer DSC-7, and thermogravimetric analysis was accomplished on a Perkin-Elmer TGA-2. Photolysis was conducted with a 450 watt high pressure mercury Hanovia lamp.

Materials. Distilled deionized water was used for most of the polymerizations. All other solvents were reagent grade and used without purification. For the polymerizations using degassed solvent, the solvent was degassed by sparging with argon or repeated freeze-pump-thaw cycles. Furan, *N*-methylmaleimide, *N*-phenylmaleimide and maleimide were purchased

from the Aldrich Chemical Company and used without further purification. Endo-**1**, and **4** were synthesized according to literature procedures.[46] $Ru^{II}(H_2O)_6tos_2$ (**2**) was prepared according to literature procedures.[31,32] $[Ir(COD)(PCy_3)(py)]^+PF_6^-$ (Crabtree's catalyst) was kindly supplied by Crabtree's group.

Preparation of *exo*-*N*-methyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (1). A mixture of 13.1 mL of furan (12.3 g, 0.18 mol), and 10 g (0.09 mol) of N-methylmaleimide in 50 mL of Et_2O was degassed in a large heavy-walled flask equipped with a Teflon seal. The flask was sealed under vacuum and then heated to 90 °C in an oil bath for 4 h. White crystals formed in the reaction flask upon cooling. The crystals were collected, washed with Et_2O, and dried under dynamic vacuum (95% yield). The product was determined to be pure exo isomer by ^1H NMR spectroscopy. Further purification of this product can be accomplished by recrystallization from water or ethyl acetate. Mp: 142-143 °C; IR (KBr pellet): 3445, 1761, 1691, 1442, 1286, 1019, 881 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.81 (s, 2H), 2.95 (s, 3H), 5.23 (s, 2H), 6.48 (s, 2H); ^{13}C NMR (D_2O): δ 179.63, 137.11, 81.67, 48.21, 25.58; Anal. Calcd. for $C_9H_9NO_4$: C, 59.64; H, 5.06; N, 7.82. Found: C, 60.23; H, 4.87; N, 7.89.

General Polymerization Procedure. In a typical polymerization the monomer (**1**, 1.09 g, 6.07 mmol), catalyst (**2**, 22 mg, 0.04 mmol), and a magnetic stir bar were degassed as solids in a Schlenk flask for 1 h. Degassed water or a water/ethanol solution (15 mL) was transferred via syringe into the Schlenk flask through a septum under argon. The reaction mixture was allowed to stir under argon for 1 h. The flask was then placed in an oil-bath at 55-60 °C. A

white precipitate formed after 3-5 min. After 3 h, the flask was removed from the oil bath, and the polymer was filtered through a glass frit and washed successively with water and acetone. The polymer was then dried under dynamic vacuum overnight at RT. Poly-**1** can be further purified by dissolution in methylene chloride and precipitation from methanol. Yields ranged from 85-98 %. IR (film): 3618, 3466, 2951, 2869, 1779, 1704, 1436, 1382, 1282, 1130, 1031, 970, 919, 734 cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.03 (bs), 5.78 (bs), 4.97 (bs), 4.47 (bs), 3.33 (bs), 2.96 (bs); assignments are shown in Figure 2; ^{13}C NMR (CD_2Cl_2): δ 176.09, 132.81, 131.48, 81.14, 77.49, 52.85, 25.22; Anal. Calcd. for $C_9H_9NO_4$: C, 59.64; H, 5.06; N, 7.82. Found: C, 57.32; H, 5.24; N, 7.41.

Hydrogenation of Poly-1 Employing Crabtree's Catalyst.[43] In a typical hydrogenation experiment, poly-**1** was dissolved in methylene chloride in a flask equipped with a Teflon seal and degassed via freeze-pump-thaw cycles. Crabtree's catalyst, $[Ir(COD)(PCy_3)(py)]^+PF_6^-$, was introduced under argon in an amount such that the molar ratio of carbon-carbon double bonds to [Ir] was between 40 and 100. The solution was then stirred under an atmosphere of hydrogen at room temperature for 1 h. The polymer was precipitated from methanol and dried under dynamic vacuum overnight. The yield was greater than 90% in all cases. ^1H NMR ($CDCl_3$): δ 3.84 (bs), 3.11 (bs), 2.93 (bs), 1.92 (bs); ^{13}C NMR ($CDCl_3$): δ 176.27, 81.13, 80.91, 52.25, 31.69, 31.16, 30.86, 25.44, 24.87.

Exchange of Bound 1 for *N*-methylmaleimide. In a small flask, 54 mg of **1** (0.30 mmol) was heated in 0.7 mL of D_2O in the presence of 6.7 mg of $Ru^{II}(H_2O)_6tos_2$ (0.01 mmol) under argon for 2.5 h. The polymer that formed was pushed down to the bottom of the flask, and the yellow polymerization

solution was transferred via pipet into an NMR tube. The ^{1}H NMR spectrum was acquired. *N*-methylmaleimide (13 mg, 0.01 mmol, 1 equiv) was then introduced into the NMR tube and the tube was placed in an oil bath at 55 °C for 30 min. The tube was removed and another ^{1}H NMR spectrum was acquired. This procedure was repeated after 6.5 more hours in the oil bath. The initial olefin complex, **3**, was completely converted into the *N*-methylmaleimide complex. The chemical shifts of **3** and Ru-*N*-methylmaleimide are as follows: **3**; ^{1}H NMR (D_2O): δ 5.19 (s, 2H), 5.08 (s, 2H), 3.59 (s, 3H), 2.78 (s, 2H). Ru-*N*-methylmaleimide; ^{1}H NMR (D_2O): δ 5.97 (s, 2H), 2.55 (s, 2H).

References and Notes

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acetate. ^{1}H NMR (DMSO-d_6): 11.15 (bs, 1H), 6.51 (s, 2H), 5.10 (s, 2H), 2.83 (s, 2H).

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(36) The increase in molecular weight of the polymer obtained under the rigorous exclusion of oxygen may be the result of a reduced number of initiation events or termination events (or both) when the oxygen concentration is very small. It has been reported that small amounts of oxygen actually increased the rate of polymerization of norbornene using a variety of ruthenium based catalysts. See: Ivin, K.J., Reddy, B.S.R., Rooney, J.J. *J. Chem. Soc., Chem. Comm.* **1981**, 1062-1064.

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Chapter 2

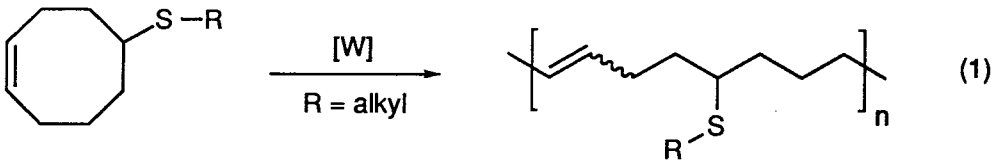
Polymerization of Functionalized Cyclooctenes by a Ruthenium-Based Metathesis Catalyst

Abstract: The ring-opening metathesis polymerization (ROMP) of a variety of 5-substituted cyclooctenes by the well-defined metathesis catalyst $(PCy_3)_2(Cl)_2RuCHCHCPh_2$ (**1**) was accomplished. The polymers were obtained in moderate to good yields. The structures of the polymers were confirmed by IR, ^1H NMR, and ^{13}C NMR spectroscopies. The molecular weight of one of the derivatives was controlled by varying the monomer to catalyst ratio and by the addition of a chain transfer agent to the polymerization solution. The thermal properties of the polymers are reported.

Introduction

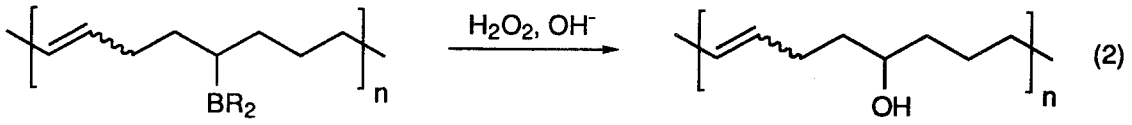
The incorporation of functional groups (e.g. esters, nitriles, halogens, alcohols) into the backbones of polymers produced by ring-opening metathesis polymerization (ROMP) has received a great deal of attention of late.[1,2] The increased tolerance of newly-developed early[3-5] and late[6,7] transition metal catalysts toward polar functionalities has facilitated much of the progress. Although there has been considerable success in the ROMP of functionalized cyclic olefins, in most of the reports the monomers employed contain the highly strained bicyclic olefin norbornene. The incorporation of a functional group into a monomer which contains a highly reactive (i.e. strained) cyclic olefin allows the use of a less active catalyst for polymerization. With most early transition metal catalysts, the tolerance of polar functional groups is inversely proportional to the metathesis activity of the catalyst. Polymerization of less-strained cyclic olefins requires the use of a more active catalyst and thus precludes the incorporation of functional groups into the monomer. As a result, there are comparatively few reports concerning the ROMP of less-strained monocyclic olefins which contain functional groups.[8-11]

Substituted cyclooctenes represent a particularly interesting class of monomers. Their ROMP products are formally terpolymers of butadiene, ethylene, and a substituted ethylene. For example, Basset recently demonstrated the ROMP of a number of 5-alkylthiocyclooctenes by a well-defined tungsten-based metathesis catalyst (eq 1).[12] This is one of the first reports on the metathesis of sulfur containing olefins. The resulting polymers can be considered terpolymers of butadiene, ethylene and vinyl sulfides. Also,



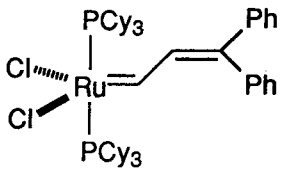
(1)

Chung reported the polymerization of an alkyl boron substituted cyclooctene.[13] The hydroxyl group is masked as a trialkylboron since the catalyst used in this procedure will preferentially react with the hydroxyl group over the olefin. Complete oxidation and hydrolysis of the corresponding borane substituted polymer yields a terpolymer of butadiene, ethylene, and vinyl alcohol (eq 2).[14] The thermal stability of this polymer and its saturated derivatives was significantly better than that of poly(vinyl alcohol).



(2)

Recently we described the synthesis of a discrete ruthenium-based metathesis catalyst (**1**) that was active for the polymerization of cyclopentene, cyclooctene, and 1,5-cyclooctadiene (**COD**).[15] In addition, **1** was active for the metathesis of functionalized acyclic olefins.[15,16] In this chapter, the polymerization of cyclooctenes with pendant functional groups catalyzed by **1** is described.



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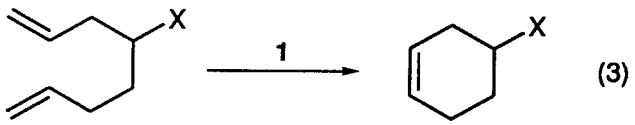
Results and Discussion

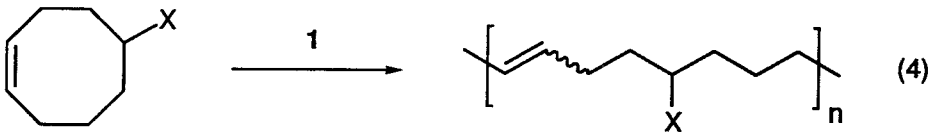
The ruthenium-based metathesis catalyst **1** has been shown to be tolerant of wide variety of functional groups.[15] This well-defined catalyst will preferentially react with olefins in the presence of polar functional groups such as alcohols, aldehydes, ketones, esters, and ammonium salts. This reactivity has been exploited in the metathesis of such substrates as methyl oleate,[15] and has been particularly useful in the catalytic ring closing metathesis of functionalized dienes (eq 3).[16]



(3)

X = CO_2H, CH_2OH, CHO

The ability of **1** to catalyze the metathesis of functionalized acyclic olefins as well as the ROMP of relatively low-strain cyclic olefins prompted this investigation on the ROMP of functionalized cyclooctenes (eq 4).



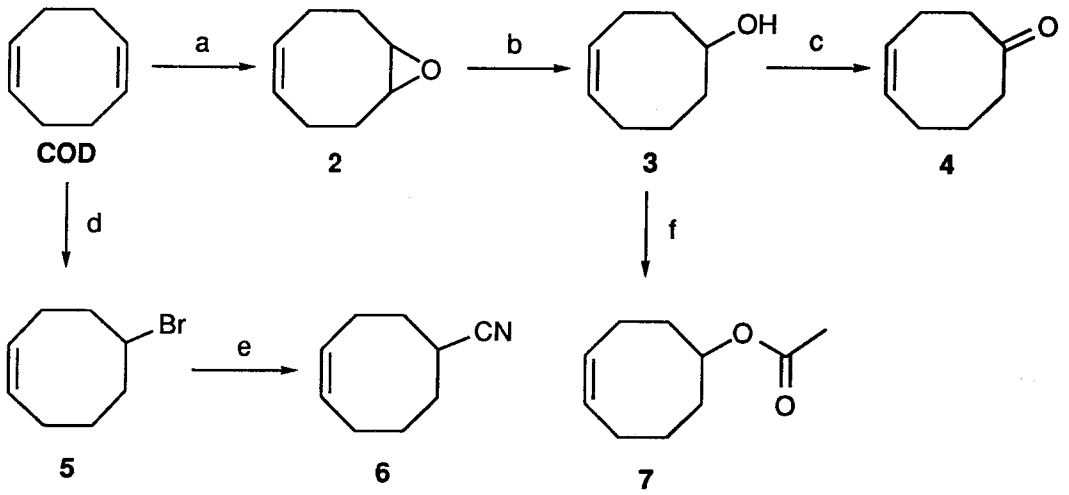
(4)

X = OH,  , Br, $OCOCH_3$

Monomer Synthesis. The synthesis of the substituted cyclooctenes employed in this work were easily performed on a multigram scale from

cyclooctadiene (**COD**), and all compounds were isolated in moderate to good yield. The synthetic routes to these compounds are illustrated in Scheme 1.

Scheme 1



a) MCPBA/$CHCl_3$ (66%) b) LAH/THF (100%) c) PCC/CH_2Cl_2 (95%) d) HBr/HOAc (74%)

e) NaCN/DMSO (45%) f) $ClCOCH_3$/pyridine (100%)

All of the monomers synthesized were liquids at room temperature and were purified by distillation or chromatography. The ruthenium catalyst **1** was also easily synthesized on a multigram scale using standard Schlenk techniques.

Polymerization Procedure. In a typical polymerization, complex **1** was dissolved in a minimum amount of anhydrous, degassed CH_2Cl_2 (e.g. 15mg of **1** in 200 μL of CH_2Cl_2) and added to a vial containing the monomer and a magnetic stir bar. The polymerizations were performed under argon at either room temperature or 45 - 50 °C. The polymerizations were terminated by the addition of ethyl vinyl ether[17] and isolated by precipitation from an appropriate non-solvent. The conditions and results are shown in Table 1.

Table 1. Polymerization of Substituted Cyclooctenes by 1[a]

entry	monomer	[M]/[1]	t (h)	T (°C)	yield (%)	$10^{-3}\overline{M_n}$[b]	PDI[b]
1	3	1044	24	23	65	139	1.6
2	4	1037	72	23	47	97.9	1.8
3	5	1056	144	23	92	82.4	1.9
4	7	1044	72	23	57	96.0	1.9
5	7	1041	25	47	85	138	2.4
6	6	181	24	23	-	-	-
7	2	523	24	23	-	-	-

[a] **1** was dissolved in a minimum amount of CH_2Cl_2, added to neat monomer, and the polymerizations were performed under argon.
[b] Determined by GPC inTHF using polystyrene standards.

The polymerizations are relatively slow compared to unsubstituted monomers such as cyclooctene, **COD**, and cyclopentene.[18] Both the rate of polymerization and polymer yield are significantly increased with increased concentration of the monomer. Best results were obtained when the polymerizations were run in the minimum amount of solvent.[19] Monomers **3**, **4**, **5**, and **7** were successfully polymerized and isolated in good unoptimized yields as rubbery solids. In the case of poly-**7**, an increase in the polymerization temperature increased the yield and molecular weight of the polymer (entries 4 and 5). All of the polymers were readily soluble in common polar organic solvents (e.g. THF, chloroform, methylene chloride). Poly-**3** was soluble in THF, however significant enhancement in the solubility

was observed in a mixture of chloroform and methanol. Initial attempts to polymerize **2** and **6** failed. Presumably reaction of the epoxide in **2** (coordination or ring-opening) with **1** inhibits polymerization, but this has not been confirmed experimentally. There is precedence for the deactivation of **1** by nitriles,[20] and coordination of the nitrile in **6** to **1** is probably responsible for catalyst deactivation.

Polymer Characterization. The structures of the polymers obtained (poly-**3**, poly-**4**, poly-**5** and poly-**7**) were examined by ^{1}H NMR, ^{13}C NMR, and IR spectroscopies. All of the spectroscopic data were consistent with the repeat units shown in eq 2. The olefinic regions of the ^{1}H NMR spectra were not well resolved for poly-**4** and poly-**5**, however in the ^{1}H NMR spectra of poly-**3** and poly-**7** two overlapping signals centered at δ 5.25 and δ 5.32 respectively were assigned to cis and trans repeat units (~40% cis for poly-**3** and ~50% cis for poly-**7**). The IR spectrum of each of the polymers contained olefinic out-of-plane C-H bending absorptions for both cis (665-730 cm^{-1}) and trans (960-980 cm^{-1}) olefins consistent with the presence of both cis and trans repeat units.

The ^{13}C NMR spectra of these polymers were useful in further assigning the microstructure. In the parent polyocteneamer (i.e. from cyclooctene), the olefinic carbon resonances are only sensitive to the configuration of the adjacent sp^2 carbon and not the configuration of the next nearest double bond. This is also true for polyhepteneamer and polypenteneamer.[10] Therefore, these three polymers exhibit only two resonances (one cis and one trans) in the olefinic region of their respective ^{13}C NMR spectra. For each of the polymers synthesized in this work, the olefinic region of the ^{13}C NMR spectra contained eight resonances. Although these resonances were not definitively assigned, this multiplicity is consistent

with the presence of cis and trans double bonds as well as the presence of three possible regioisomers. The cyclooctenes are asymetrically substituted, and therefore head-to-head (HH), head-to-tail (HT), and tail-to-tail (TT) repeat units are possible. If the ^{13}C olefinic resonances are *only* sensitive to the configuration of the adjacent sp^2 carbon (analogous to the parent polyocteneamer) and to the *position* of the two nearest functional groups, then there should be eight resonances (a-h) in the absence of high regio- or stereospecificity. These different repeat units with the unique carbons labeled are shown in Figure 1.

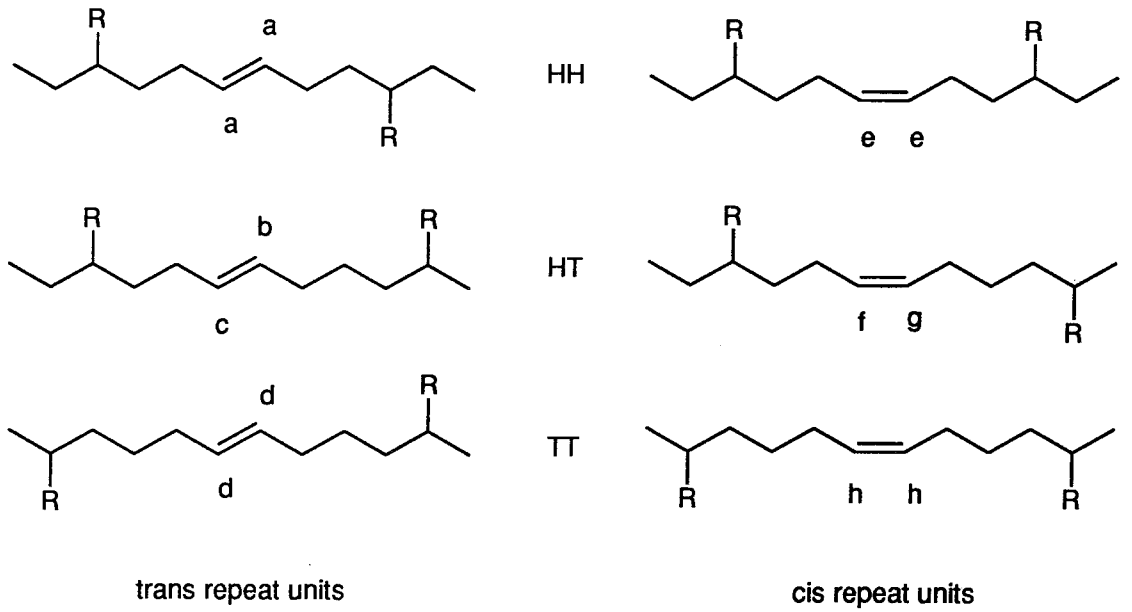
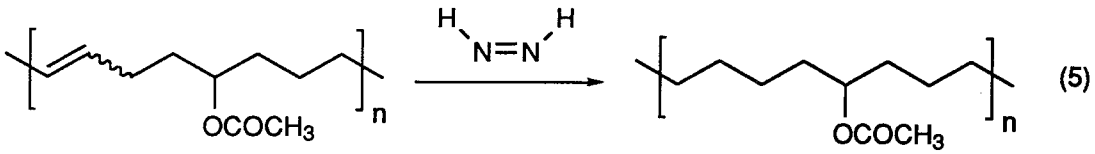


Figure 1. Possible repeat unit structures for the polymers of 5-substituted cyclooctenes.

This analysis assumes that the chemical shifts of the olefinic carbons are insensitive to relative stereochemistry of the two adjacent chiral carbons (racemic or meso diads for the HH and TT regioisomers). This is corroborated by the presence of eight resonances in the olefinic region of the ^{13}C NMR

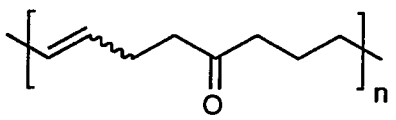
spectrum for poly-4 (Figure 2). In poly-4 there are no chiral carbons, and therefore there are a *maximum* of 6 different repeat units (eight different carbons). If the chemical shifts of the olefinic carbons were also sensitive to meso and racemic diads, an increased number of resonances (which is *not* observed) would be expected for the polymers derived from the cyclooctene derivatives containing a chiral carbon.

To further establish the microstucture of poly-7, the fully saturated version of poly-7 was also synthesisized by stoichiometric hydrogenation with diimide (eq 5).[21]



(5)

The diimide reduction was very efficient and effective for the reduction of only the olefinic portion of the poly-7. The ^{1}H NMR spectrum (Figure 3) of this polymer is consistent with the structure shown in eq 3. The ^{13}C NMR of poly-7 simplified upon hydrogenation. There were no olefinic carbon resonances observed for the hydrogenated polymer. Two equally intense resonances were observed for the methine carbon (δ 74.38 and δ 74.34) indicating, again, a regioirregular microstructure. Only in the case of a perfectly head-to-tail arrangement of repeat units would one resonance for the methine carbons be expected. Although the regiochemistry of both the parent polymer (poly-7) and its hydrogenated version were determined to be irregular, the polyethylene/polyvinylacetate copolymer (hydrogenated poly-7) contains an acetate group every eight carbons on average. This is also the case for the other isolated polymers.



poly-4 (HT, TT, HH)

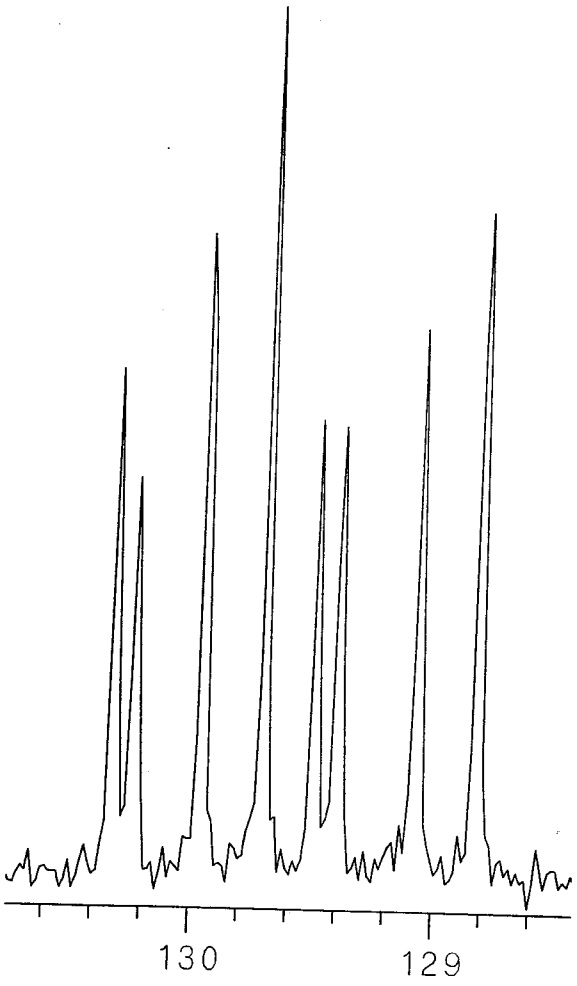
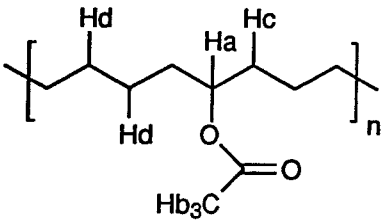


Figure 2. The olefinic region of the ^{13}C NMR spectrum (75 MHz, $CDCl_3$) for poly-4 (scale is in ppm).



hydrogenated poly-7

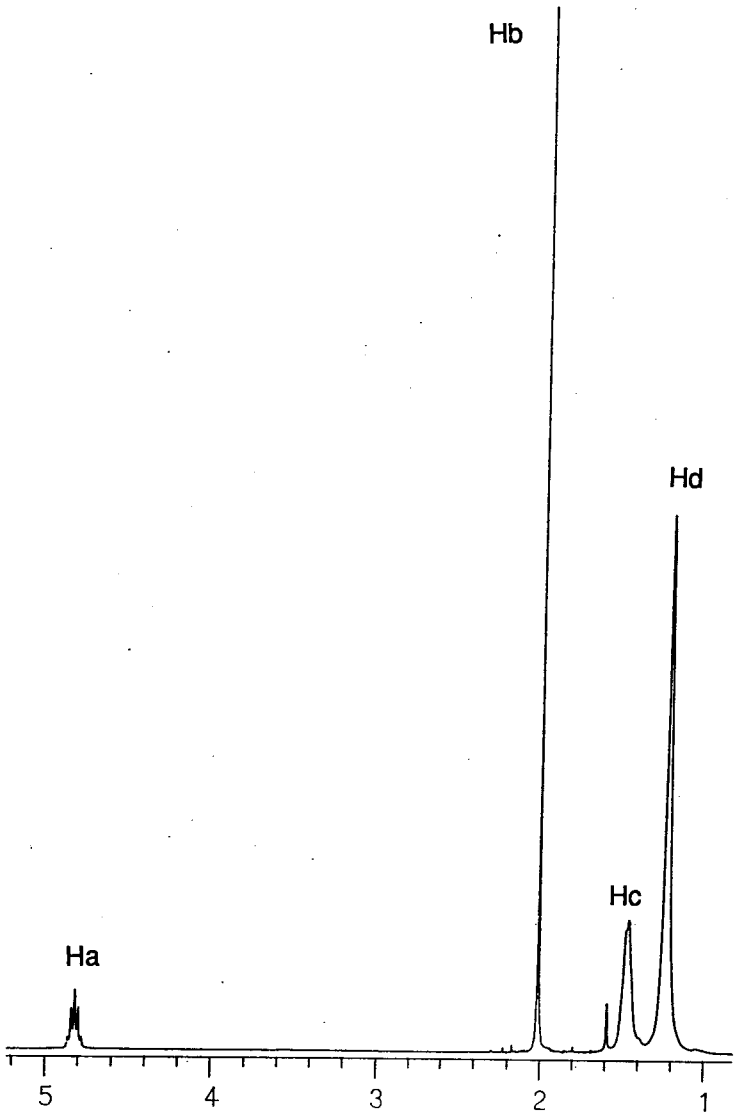


Figure 3. ^1H NMR spectrum (300 MHz, $CDCl_3$) of hydrogenated poly-7 (scale is in ppm).

The lack of regiospecificity is not surprising in the ROMP of these 5-substituted cyclooctenes. The substituent on the cyclooctene ring is presumably too far away from the double bond to influence the orientation of the catalyst during the propagation step. This is corroborated by the preferred conformation of 5-substituted cyclooctenes. The dominant conformation of 5-hydroxy-1-cyclooctene (3) and the corresponding tosylate (as determined by NMR spectroscopy) is shown in Figure 4.[22]

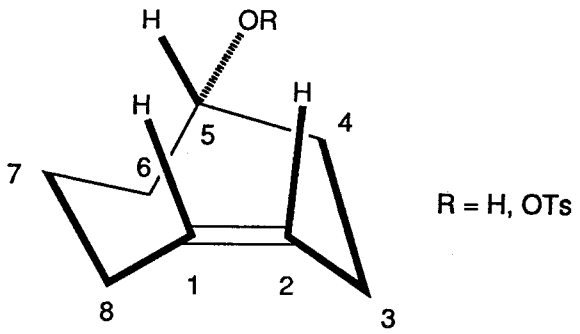


Figure 4. Preferred conformation of two 5-substituted cyclooctenes.

The large substitutent on carbon 5 occupies the outside or pseudo-equatorial position on the ring in a chair-boat type conformation. This conformation also suggests that in the propagation step, the preferred double bond orientation would be trans (i.e. with the propagating polymer directed up or away from the bottom portion of the ring ; carbons 3 and 8). In fact, high trans polymers are observed in the polymerization of cyclooctene (which has a similar conformation) with **1**.[15] However, the regiospecificity and stereospecificity in the polymerization of the 5-substituted cyclooctenes described in this work cannot be rationalized based on the propagation step alone. Interchain metathesis results in not only a broadening of molecular

weight distribution, but also in an equilibration of the regioisomers and double bond orientations in the repeat unit. It is difficult from the data presented here to determine whether the lack of regiospecificity is inherent in the mechanism or results from subsequent isomerization.

The molecular weights of the polymers obtained were generally high, and the polydispersities (PDI's) were between 1.6 and 2.4. Regulation of the molecular weight of poly-**7** was investigated. Although polymerizations catalyzed by **1** are not strictly living due to facile chain transfer to polymer, the total number of polymer chains should be determined by the catalyst concentration and should remain constant. The number average molecular weight of the polymer should therefore be controllable by varying the monomer to catalyst ratio. Indeed, an increase in molecular weight ($\overline{M_n}$) was observed with increasing monomer to catalyst ratio (Table 2). The relationship between [M]/[C] and $\overline{M_n}$ is linear at relatively low monomer to catalyst ratios. The molecular weight of poly-**7** can also be lowered if the polymerization of **7** is carried out in the presence of an acyclic olefin such as *cis*-3-hexene (Table 2, entries 5 and 6).[23] The *cis*-3-hexene acts as a chain transfer agent in this polymerization.[10] The use of a chain transfer agent allows the synthesis of relatively low molecular weight materials while keeping the monomer to catalyst ratio high (entry 6). The molecular weight is determined by the monomer to chain transfer agent (*cis*-hexene) ratio. Increasing this ratio approximately twofold (from 81 [entry 5] to 193 [entry 6]) results in a twofold increase in the number average molecular weight of the polymer (from 24.4K to 49.1K).

Polymer Properties. The thermal properties of the polymers were analyzed by DSC and TGA. The T_g, T_m, T_{rc} and the temperature at 10% weight

Table 2. Molecular Weight Regulation of Poly-7[a]

sample	[M]/[C]	$10^{-3}\overline{M_n}^b$	PDI[b]	yield (%)
1	247	64.1	1.9	88
2	540	96.3	2.1	92
3	1082	126	2.0	90
4	2244	129	2.0	87
5[c]	2688	24.4	1.7	55
6[d]	4700	49.1	1.8	67

[a] Polymerization performed at 50 °C for 24 h.
[b] Determined by GPC in THF using polystyrene standards.
[c] Polymerized in the presence of *cis*-3-hexene ([M] / [*cis*-3-hexene] = 81).
[d] Polymerized in the presence of *cis*-3-hexene ([M] / [*cis*-3-hexene] = 193).

loss (T_d) are given for each polymer in Table 3. The T_g values for all of the polymers were found to be below room temperature. With the exception of poly-4, no other transitions or reactions were observed by DSC below 100 °C for the polymers. An interesting result is found by comparing the T_g values of poly-7 and hydrogenated poly-7. The T_g values of poly-7 and hydrogenated poly-7 were found to be identical. This behavior has also been observed for polyisoprene and its hydrogenated version (polypropylene-*alt*-polyethylene).[24]

Both poly-7 and hydrogenated poly-7 have similar decompostion temperatures and undergo a two-stage weight loss (i.e. a weight loss, then a plateau followed by second weight loss). Both polymers lose approximately 37

Table 3. Polymer Thermal Properties[a]

sample	T_g (°C)	T_m, T_{rc} (°C)	T_d (°C)
poly-3	10	b	386
poly-4	-58	34, 2	404
poly-5	-54	b	285
poly-7	-38	b	349
hydrogenated poly-7	-38	b	345

[a] All values were obtained under an atmosphere of argon at a scan rate of 10 °C/min.

[b] No other transition or reaction was observed between the T_g and 100 °C by DSC.

± 2% of their weight between 300 and 400 °C, and the remaining weight is lost in a subsequent step beginning at ~430 °C. The initial weight loss is accompanied by an exothermic transition in the DSC for both of the polymers. These results are consistent with the thermal elimination of acetic acid (36% of the repeat unit weight) followed by complete decomposition. In poly-**5** a similar two-stage weight loss is observed. Poly-**5** loses ~41% of its weight between 196 and 374 °C followed by further decomposition beginning at ~430 °C. Elimination of HBr would result in a 43% weight loss and is thought to be the initial decomposition step.

Poly-**4** (CO every eight carbons) has a structure that is intermediate between the perfectly alternating ethylene/carbon monoxide copolymers (CO every three carbons) and the biodegradable random copolymers of ethylene

and carbon monoxide (CO every 100 carbons). Poly-**4** was the only polymer that exhibited a melting point (T_m = 34 °C). This is surprising since the microstructure of the poly-**4** was determined to be irregular. It appears that there is enough regularity in the sample to induce some degree of crystallization.[25] The melt transition is reversible, and the T_{rc} was determined to be 2 °C.

Poly-**3** and its saturated version is related to the commercially important polyvinylalcohol. The T_g and T_d of poly-**3** were very close to the values reported for Chung's polymer of similar structure obtained via a hydroboration/oxidation procedure. Chung reported a T_g of 11 °C and the onset of thermal decoposition to be 430 °C.[13] However, inspection of Chung's data reveals that the polymer sample lost ~20% of its weight at 430 °C. Unlike Chung's[13] synthesis, the preparation of poly-**3** can be accomplished in one step from **3** to yield the polyethylene, polybutadiene, polyvinylalcohol terpolymer.

Conclusions

The successful ROMP of four cyclooctenes substituted with polar functional groups by the ruthenium based metathesis catalyst **1** has been demonstrated. The polymers were isolated in good yields and their structures were investigated by ^{1}H NMR, ^{13}C NMR and IR spectroscopies. Molecular weights of the polymers were generally high, and predictable molecular weight regulation was demonstrated for one of the derivatives (poly-**7**). Although the regiochemistry and stereochemistry of the repeat units in these polymers were determined to be random, there is one functional group every eight carbons in these polymers. The thermal properties of all the polymers and the mechanical properties of one of the derivatives (poly-**7**) were determined. Three of the polymers synthesized have structures similar to commercially important copolymers of ethylene; namely ethylene/CO, ethylene/vinyl alcohol, ethylene/vinyl acetate copolymers.[26] This work represents one of the few successful metathesis polymerizations of functionally substituted cyclooctenes. The success of the polymerization is a direct result of the preferential reactivity of **1** towards olefins in the presence of polar functional groups.

Experimental Section

General Considerations. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4Å molecular sieves (Linde). NMR spectra were recorded on a JEOL GX-400 spectrometer (399.65 MHz ^{1}H, 100.40 MHz ^{13}C) or a GE QE-300 Plus (300.10 MHz ^{1}H; 75.49 MHz ^{13}C) spectrometer. Gas chromatographic analysis was performed on a HP-5890 Series II Gas Chromatograph with an SE-30 capillary column. Chemical shift are reported in ppm relative to the solvent resonances. IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. Gel permeation chromatographs were obtained on a HPLC system utilizing an Altex Model 110A pump, a Rheodyne model 7125 injector with a 100 μL injection loop, two American Polymer Standards 10 micron mixed bed columns, and a Knauer differential-refractometer; tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL/min. The molecular weights and polydispersities are reported versus monodisperse polystyrene standards. Differential scanning calorimetry was performed on a Perkin-Elmer DSC-7, and thermogravimetric analysis was accomplished on a Perkin-Elmer TGA-2. Elemental analysis was performed by Fenton Harvey at the California Institute of Technology Elemental Analysis Facility.

Materials. The methylene chloride used in the polymerizations was distilled from CaH_2 under vacuum. All other solvents were reagent grade and used without purification. Pyridinium chlorochromate, sodium cyanide, *p*-toluenesulfonhydrazide, *m*-chloroperbenzoic acid were purchased from the Aldrich Chemical Company and used without further purification.

Preparation of cyclooctadiene monoepoxide (2). A solution of 100 g of 55% *m*-chloroperbenzoic acid (319 mmol) in 900 mL of chloroform was added dropwise over 2 h to 42.8 g of neat 1,5-cyclooctadiene (396 mmol) with stirring. This mixture was allowed to stir at room temperature for 12 h and subsequently filtered to remove the *m*-chlorobenzoic acid. The chloroform layer was washed with aqueous sodium bisulfite, sodium bicarbonate, and sodium chloride solutions. The organic layer was concentrated and purified by column chromatography (silica, 90/10 hexane/ethyl acetate) to yield 26 g (66%) of a clear oil. IR (neat): 2954, 1485, 1446, 938, 862 cm^{-1}; ^1H NMR (C_6D_6): δ 5.40 (t, 2H), 2.75 (t, 2H), 1.8 (m, 8H).

Preparation of 5-hydroxy-1-cyclooctene (3). A 1M THF solution of LAH (44 mL, 44 mmol) was added slowly via syringe to 10.8 g of **2** (87 mmol) in 80 mL of dry THF at room temperature. The reaction was stirred overnight at room temperature under argon, cooled to 0 °C, and quenched with water. The salts were filtered and washed with Et_2O and the organic fractions were concentrated. The resulting oil was purified by column chromatography (silica, 70/30 hexane/ethyl acetate) to yield 10.5 g (95%) of a colorless oil. GC purity 99.6%; ^1H NMR ($CDCl_3$): δ 5.63 (m, 2H), 3.78 (m, 1H), 1.4-2.4 (m, 11H); ^{13}C NMR ($CDCl_3$): δ 130.13, 129.55, 72.75, 37.74, 36.27, 25.64, 24.85, 22.75.

Preparation of cyclooct-1-ene-5-one (4). A solution of 4.0 g of **3** (317 mmol) in 50 mL of dry CH_2Cl_2 was added to a 10.2 g of pyridinium chlorochromate (474 mmol) in 60 mL of dry CH_2Cl_2 at room temperature and was allowed to stir for 5 h at room temperature. The reaction mixture was

diluted with 60 mL of Et_2O and filtered. The black chromium salts were washed with Et_2O, and the Et_2O washes were combined and concentrated. The resulting brown oil was purified by column chromatography (silica, 80/20 hexane/ethyl acetate) to yield a colorless oil in high yield. ^1H NMR ($CDCl_3$): δ 5.69 (m, 2H), 2.44 (m, 6H), 2.16 (m, 2H), 1.58 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 214.81, 130.23, 130.76, 47.28, 40.38, 26.32, 23.94, 21.83.

Preparation of 5-bromo-1-cyclooctene (5). 5 was synthesized according to the procedure described by Ashby in 74% yield.[27] ^1H NMR ($CDCl_3$): δ 5.61 (m, 2H), 4.29 (m, 1H), 2.5-1.9 (m, 8H) 1.71 (m, 1H), 1.52 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 129.55, 129.15, 55.65, 39.73, 37.09, 27.00, 25.24, 25.16.

Preparation of 5-cyano-1-cyclooctene (6). A mixture of 32 g of sodium cyanide (653 mmol), 25 g of 5 (132 mmol) and 125 mL of DMSO was placed in a round-bottom flask equipped with a condenser. The mixture was heated to 110 °C under argon for 2 h, cooled to room temperature, and poured into 200 mL of water. The resulting solution was extracted with Et_2O and the combined extracts were washed with saturated aqueous LiCl. The solvent was removed under reduced pressure to yield a yellow oil which was further purified by column chromatography (silica, 90/10 hexane/ethyl acetate) to yield 8.1 g (45%) of 5-cyano-1-cyclooctene. ^1H NMR ($CDCl_3$): δ 5.66 (m, 2H), 2.74 (m, 1H), 1.4-2.4 (m, 10H); ^{13}C NMR ($CDCl_3$): δ 130.34, 128.62, 122.99, 31.86, 29.04, 27.88, 26.68, 24.74, 23.10.

Preparation of 5-acetoxy-1-cyclooctene (7). A solution of 1.0 g of 3 (7.9 mmol) in 10 mL of dry pyridine was cooled to 0 °C. To this solution 1.36 of

acetyl chloride (17.4 mmol) was added over 15 min. The reaction was allowed to warm to room temperature and stirred for an additional 1 h. The reaction mixture was diluted with Et_2O and washed with 1M HCl, saturated aqueous $NaHCO_3$, and water. The organic layer was dried with $MgSO_4$ and concentrated to yield 1.3 g (100%) of a slightly yellow oil. This oil can be further purified by distillation from CaH_2 under reduced pressure (95 °C at 10 mmHg). ^1H NMR ($CDCl_3$): δ 5.63 (m, 2H), 4.79 (m, 1H), 2.31 (m, 1H), 2.13 (m, 3H), 1.99 (s, 3H), 1.84 (m, 2H), 1.69 (m, 1H), 1.57 (m, 3H); ^{13}C NMR ($CDCl_3$): δ 170.43, 129.78, 129.58, 75.63, 33.71, 33.65, 21.47, 22.31, 24.80, 25.52. Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 70.82, H, 9.77.

General Polymerization Procedure. An example of the general polymerization procedure is described for the polymerization of **7**. Under an inert atmosphere, a small vial was charged with 2.6 g of degassed **7** (freeze/pump thaw cycles or an argon purge is aceptable) (15.61 mmol) and a small magnetic stir bar. A solution of 15 mg of **1** (0.015 mmol, [M]/[C] = 1041) in 200 μL of methylene chloride was added to the vial via pipette. The vial was capped and placed in an oil bath at about 45-50 °C. After 2.5 hours the red-orange solution was noticeably viscous, and after 5.5 hours the contents of the vial were solid. After 24 hours the vial was removed from the oil bath and cooled to room temperature. The cap was removed from the vial and 100 μL of ethyl vinylether, 10 mL of chloroform, and about 10 mg of 2,6-di-*tert*-butyl-4-methylphenol (ButylatedHydroxyToluene, BHT) were added to the vial. The solid dissolved, and the solution became yellow-orange. After about 12 hours of stirring, an additional 20 mL of chloroform were added to the solution, and the resulting solution was poured into about 200 mL of

methanol. The off-white solid that precipitated was stirred in the methanol until it appeared free of color. The white solid was isolated and dried overnight under vacuum to yield 2.2 g (85%).

Hydrogenation of poly-7. 1.2 g of poly-7 (7.2 mmol of olefin) was dissolved in 40 mL of hot *o*-xylene (~ 80 °C). The solution was cooled down to ~ 40 °C, 3.0 g of *p*-toluenesulfonhydrazide (16.1 mmol) and 3.1 g of tributyl amine (16.2 mmol) were added. The reaction mixture was heated at reflux for 5 h, allowed to cool to room temperature, and extracted with water (4 x 40 mL). The orange organic layer was poured into methanol, and the polymer precipitated. The polymer was isolated, dissolved in toluene, reprecipitated in methanol, isolated, and dried under vacuum to give 1.0 g (84 %) of light yellow, clear solid.

Polymer Characterization. The polymers were characterized by IR (as thin films on a NaCl plate), ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy, and C,H analysis. The data are presented below.

Poly-**3**. IR: 3358, 3002, 2930, 2849, 1651, 1455, 1337, 1079, 961, 710 cm^{-1}; ^{1}H NMR ($CDCl_3/CD_3OD$): δ 5.25 (bm, 2H), 3.68 (bs, 1H), 1.92 (bm, 4H), 1.33 (bs, 6H); ^{13}C NMR ($CDCl_3/CD_3OD$): δ 129.84, 129.65, 129.42, 129.37, 129.3 (shoulder), 129.27, 129.17, 129.05, 70.36, 70.26, 70.16, 48.61, 48.39, 48.18, 47.97, 47.75, 47.54, 47.32, 36.65, 36.57, 36.26, 36.21, 36.12, 32.02, 28.20, 26.65, 26.59, 26.54, 25.19, 25.05, 22.95, 22.92, 22.79; Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.30; H, 11.12.

Poly-4. IR: 3006, 2933, 1711, 1439, 1409, 1369, 1096, 971, 724 cm $^{-1}$; ^{1}H NMR ($CDCl_3$): δ 5.32 (bs, 2H), 2.39 (bs, 4H), 2.23 (bs, 2H), 1.97 (bs, 2H), 1.59 (bs, 2H); ^{13}C NMR ($CDCl_3$): δ 210.39, 210.36, 210.31, 210.26, 130.31, 130.23, 129.95, 129.70, 129.49, 129.39, 129.07, 128.81, 42.50, 42.46, 42.41, 42.22, 42.15, 42.12, 42.07, 42.03, 31.92, 31.86, 26.71, 26.65, 26.57, 26.54, 23.60, 23.56, 23.47, 23.37, 21.57, 21.53; Anal. Calcd. for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.17; H, 9.97.

Poly-5. IR: 3004, 2935, 2856, 1442, 1299, 1227, 968, 729, 617, 533 cm $^{-1}$; ^{1}H NMR ($CDCl_3$): δ 5.42 (bm, 2H), 3.99 (bs, 1H), 1.4-2.2 (bm, 10H); ^{13}C NMR ($CDCl_3$): δ 130.94, 130.56, 130.23, 129.82, 129.73, 129.36, 129.09, 128.54, 57.75, 38.95, 38.83, 38.69, 38.57, 32.64, 31.90, 30.55, 27.59, 27.39, 26.67, 26.58, 25.52, 25.45; Anal. Calcd. for $C_8H_{13}Br$: C, 50.82; H, 6.93. Found: C, 52.96; H, 7.32.

Poly-7. IR: 3005, 2938, 2860, 1740, 1438, 1374, 1244, 1021, 968, 728, 608 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.32 (bm, 2H), 4.84 (bs, 1H), 1.9 (bm, 7H), 1.51 (bm, 4H), 1.32 (bm, 2H); ^{13}C NMR ($CDCl_3$): δ 170.78, 130.35, 130.19, 129.88, 129.77, 129.68, 129.60, 129.31, 129.10, 73.76, 73.73, 34.06, 34.00, 33.93, 33.81, 33.77, 33.64, 32.39, 28.42, 27.00, 26.96, 25.32, 25.24, 25.19, 23.20, 23.16, 21.25; Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.58. Found: C, 71.19; H, 9.63.

Hydrogenated poly-7. IR: 2829, 2856, 1737, 1464, 1441, 1372, 1243, 1021 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 4.82 (m, 1H), 2.01 (s, 3H), 1.46 (bs, 4H), 1.22 (bs, 10H); ^{13}C NMR ($CDCl_3$): δ 170.91, 74.38, 74.34, 34.15, 29.52, 29.48, 25.32, 25.26, 21.27; Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.66; H, 10.66.

Appendix

Poly-7 and hydrogenated poly-7 are similar in structure to commercially useful ethylene/vinyl actetate copolymers[26,28] and therefore the mechanical properties of poly-7 and hydrogenated poly-7 (50.6 weight % vinyl acetate) were investigated and are shown in Table 4.[29]

Table 4. Mechanical Properties of Poly-7 and Hydrogenated Poly-7

property		poly-7	hydr. poly-7
stress (lb/in^2)	peak	16.5	33.5
	break	6.5	15.5
strain (%)	peak	42.3	51.2
	break	246	262
toughness ($in\text{-}lb/in^3$)		29.5	63.5
energy at break (lbs-in)		0.093	0.223
Young's modulus ($lb/in^2 \times 10^{-3}$)		0.15	0.26

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Chapter 3

The Synthesis of Hydroxytelechelic Polybutadiene by Ring-Opening Metathesis Polymerization[1]

Abstract: The ring-opening metathesis polymerization (ROMP) of cyclooctadiene (**COD**) by well-defined metathesis catalysts based on tungsten, molybdenum and ruthenium in the presence of a variety of chain transfer agents (CTAs) is described. Expressions for the theoretical molecular weight and functionality were derived for this type of ROMP system. The hydroxytelechelic polybutadienes (HTPBDs) synthesized contain one type of regiochemistry in the repeat unit (1,4) and one type of alcoholic endgroup. The molecular weight of the HTPBDs was controlled by the ratio of **COD** to CTA and number average functionalities that approached 2.0 were obtained at high CTA to catalyst ratios.

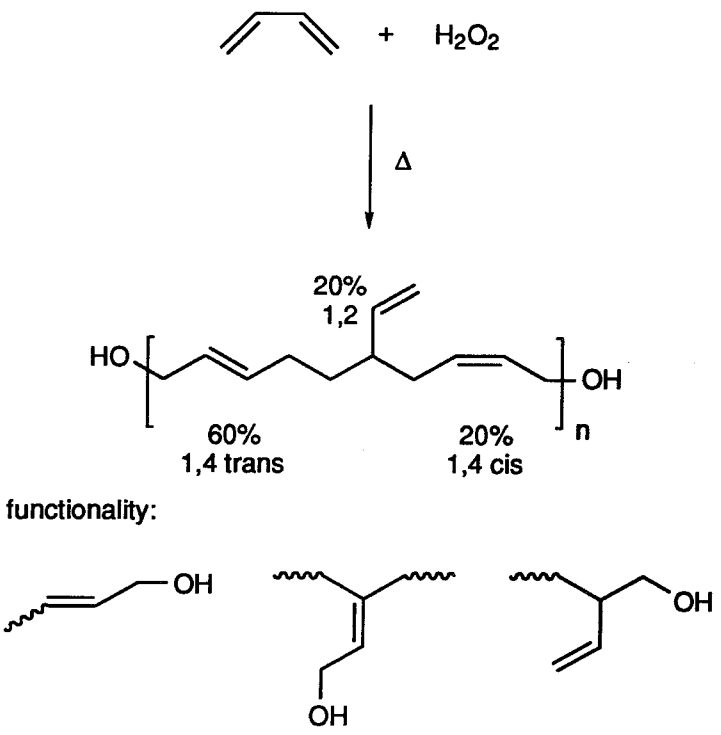
Introduction

Telechelic Polymers. Telechelic polymers are low-molecular-weight macromolecules that possess a reactive endgroup at each end of the chain.[2] They are useful materials for chain extension processes, block copolymer synthesis, reaction injection molding, and network formation.[2,3] It is often advantageous from a processing standpoint to use telechelics as liquid prepolymers that will be employed in a subsequent step polymerization with another telechelic or difunctional monomer. For example, telechelic polyethers and polyesters have been used extensively in the polyurethane industry for the formation of "reactive prepolymers."[4] The synthesis of telechelic polymers requires the placement of a specified functional group at each end of a polymer chain. Because of the potential and established utility of telechelic polymers, most of the classical polymer synthesis techniques (e.g. step-condensation, cationic, anionic, and radical) have been utilized in their synthesis.[2] As a result most common polymers have been synthesized with reactive endgroups. For example, telechelic polyesters, polybutadienes, polystyrenes, polyisoprenes, and polyvinylalcohols with a variety of endgroups have been prepared.[2]

A particularly useful telechelic polymer is hydroxytelechelic polybutadiene (HTPBD). Commercially produced HTPBD has found a variety of industrial applications.[4-6] HTPBD is mostly used as a polyol in the synthesis of polyurethane elastomers.[4] Polyurethanes that contain HTPBD have many useful properties including low temperature flexibility, hydrolytic stability, and high electrical resistance.[5] These polyurethanes are used as rocket propellant binders, electronic component encapsulents, adhesives, and

sealants. Commercially produced HTPBD[7,8] is obtained by the free-radical polymerization of 1,3-butadiene by hydrogen peroxide (Scheme 1).

Scheme 1



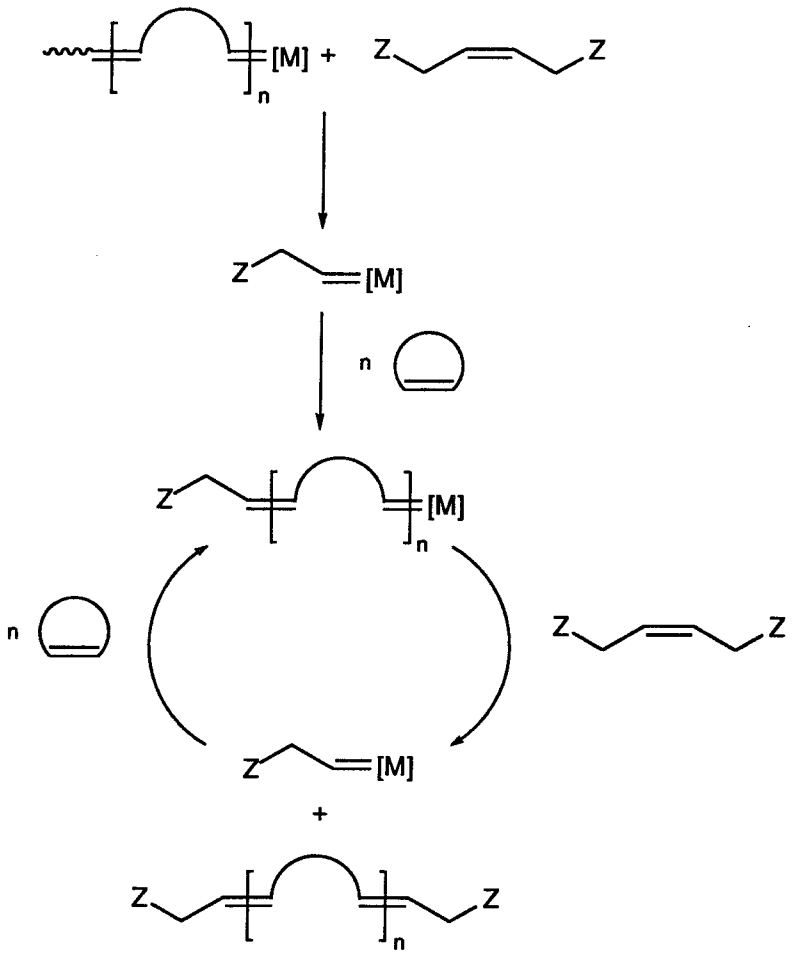
HTPBD produced by this method contains a mixture of 1,4 and 1,2 repeat units and at least three types of hydroxy endgroups.[9-12] Although the average functionality (number of functional groups per chain) of HTPBD obtained from this radical polymerization is typically greater than 2,[10,13] termination by disproportionation can lead to monofunctional polymers. These monofunctional telechelics are detrimental to the production of high molecular weight polymers in a subsequent step growth polymerization. As with most free radical polymerizations, the ease of HTPBD preparation by this method is balanced by the lack of regiospecificity and endgroup specificity.

There can be significant differences in molecular weight distributions, functionality distributions, and regiochemistry between HTPBDs produced by radical polymerizations under different circumstances.[11] Also, batch-to-batch variability in the manufacture of HTPBD results in unpredictable polymer properties.[14] These differences can affect mechanical properties, pot life, and cure behavior of a corresponding polyurethane.[14] The ability to systematically tailor the structure of HTPBD (both the regiochemistry and functionality) would allow a fundamental understanding of structure-property relationships in the polymer and derived copolymers. Living anionic polymerization techniques offer a potential solution, and progress has been made in this area.[2,3,15,16]Also, Novak recently reported the endgroup modification of living bifunctional polybutadiene initiated by a bifunctional nickel catalyst.[17] Polybutadienes terminated with hydroxyl groups were synthesized and supporting evidence was given for complete conversion of the chain ends to secondary alcohols. In this chapter, the ring-opening metathesis polymerization (ROMP)[18-21] of cyclic olefins using discrete metal alkylidene catalysts is described. This is an alternative polymerization technique that is applicable to the synthesis of well-defined telechelic polymers, HTPBD in particular. This process involves the polymerization of a cyclic olefin in the presence of a difunctional acyclic olefin which acts as a chain transfer agent (CTA).

Chain Transfer in ROMP. Acyclic olefins act as CTAs to regulate the molecular weight of polymers produced by ROMP.[18] When α,ω-difunctional olefins are employed as CTAs, difunctional telechelic polymers can be synthesized.[22-31] In the chain transfer reaction with a symmetric α,ω-difunctional olefin, a propagating polymer chain is terminated with a

functional group, and the new functional group substituted metal alkylidene reacts with monomer or a preformed polymer chain and effectively transfers the active species from one chain to another. This process preserves the number of active catalyst centers and leads to symmetric telechelic polymers with a number average functionality that approaches 2.0 (Scheme 2).

Scheme 2



telechelic polymer

The only polymer endgroups that do not contain residues from the CTA are those from the initiating alkylidene and the endcapping reagent (endgroups

from termination processes). In principle, these endgroups could be chosen to match the endgroup from the CTA.

Ill-defined classical metathesis catalysts have been employed in most cases of ROMP employing a chain transfer agent (ROMP/CT) reported to date.[22-32] It is not possible either to modulate the activity of the catalyst systematically, to define the structure of the initiating alkylidene, or to control the mode of termination in these multi-component catalysts. For many classical catalysts, irreproducible activities from batch-to-batch have been observed. In addition, the Lewis acid co-catalysts typically found in these systems (e.g., AlR_3, SnR_4, or $AlClR_2$) can react with functional groups of the CTA or with the monomer itself,[33] leading to unwanted byproducts and catalyst deactivation. These problems can potentially be circumvented by the use of well-defined, Lewis acid-free metal alkylidene complexes whose structures and activities can be easily modified.[20,34-36] Furthermore, these catalysts can produce living polymer chains where there is no termination of the active catalyst center in the absence of an endcapping reagent.[20,37]

There is obviously a considerable amount of chain transfer occuring in a ROMP/CT system of this type. Therefore, by definition, it is not a living polymerization system. However, termination could ideally be kept to a minimum in the absence of fortuitous impurities or spontaneous termination. This is especially the case when well-defined metathesis catalysts are employed where functional group tolerance and longevity are often observed.[38] Therefore, after complete conversion of the monomer there are still active chain ends. Unlike chain transfer in a radical polymerization, once all of the monomer (cyclic olefin) is consumed in a ROMP/CT system, incorporation of the CTA as polymer endgroups can still be accomplished if

termination is kept to a minimum. This is because acyclic metathesis with both the polymer backbone and the chain transfer agent can still occur in the absence of monomer. This process is called metathesis degradation[18] and has recently been used in the synthesis of telechelic polybutadiene.[31] In the ideal case, the catalyst would remain active until equilibrium is reached. Because of this, chain transfer in a ROMP system employing catalysts that do not terminate over the course of the reaction is best described as a thermodynamic rather than a kinetic phenomenon. This has implications in the calculation of theoretical molecular weight and functionality for the polymers produced in an equilibrium ROMP/CT system.

Theoretical Molecular Weight in an Equilibrium ROMP/CT System. In most reports that describe the regulation of the molecular weight of a polymer produced via ROMP by the introduction of an acyclic olefin, an increase in the concentration of the acyclic olefin relative to the monomer concentration results in a decrease in the observed molecular weight of the polymer. Some authors[25,26,28] have treated the molecular weight reduction in ROMP systems in a manner similar to that for a radical polymerization with chain transfer.[39] A typical Mayo plot is made and the slope of line is defined as a chain transfer constant. Recently, Benedicto and Grubbs addressed this issue and has derived an analytical expression for the number average degree of polymerization ($\overline{X_n}$) and polydispersity index (PDI) for a *living* polymerization with chain transfer.[40] In this case, the slope of the typical Mayo plot is *not* a chain transfer constant. Here a relationship between $\overline{X_n}$ and the concentration of CTA is derived for an equilibrium ROMP/CT system.

The number average degree of polymerization $\overline{X_n}$ is defined as the

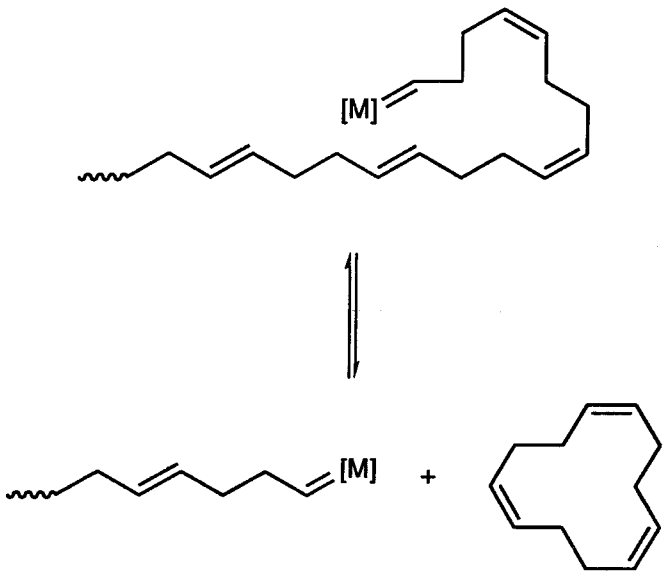
average number of structural units per polymer chain.[39] For a ROMP system in the absence of chain transfer and with complete initiation of the catalyst (C) the total number of polymer chains is equal to $[C]_o$. At time t $\overline{X_n}$ is given by

$$\overline{X_n} = \frac{[M]_o - [M]_t}{[C]_o} \quad (1)$$

where the subscripts o and t denote initial concentration and concentration at time t respectively and M denotes monomer. This is the expression for a typical living polymerization. However, even in a polymerization where intermolecular chain transfer to polymer is occurring eq 1 should still hold since the total number of chains is preserved. The polydispersity should approach 2.0 in this case.[18] The total number of *linear* chains should always be equal to the number of catalyst molecules. Any termination only decreases the total number of *active* chains. Chain transfer reactions other than chain transfer to polymer *increase* the number of linear chains in the system. However, there are no viable mechanisms for chain transfer to monomer or solvent in the ROMP of a cyclic olefin catalyzed by the aforementioned well-defined, Lewis-acid-free metal alkylidene complexes.

There are two possible chain transfer reactions that can occur. The first is chain transfer to polymer, and this reaction is divided into two categories: intermolecular chain transfer to polymer and intramolecular chain transfer to polymer. Intermolecular chain transfer to polymer is the reaction of a growing polymer chain with another chain in the system. As a result, the propagating species is transferred from one polymer chain to another, but there is no change in the total number of polymer chains (see above). Intramolecular chain transfer to polymer is classified as a backbiting reaction.

Reaction of a propagating species with a double bond in the backbone of the polymer to which it is a part of results in the formation of cyclic oligomers (eq 2).[18]



(2)

Again, there is no change in the total number of linear polymer chains, and any cyclic oligomer (including the monomer) in the reaction is treated as unreacted monomer ($[M]_t$). To keep the concentration of cyclic oligomers to a minimum, polymerizations should be run at as high a concentration of monomer as possible.[18,39]

The second type of chain transfer is the desired reaction of chain transfer to acyclic olefin. For every chain transfer reaction to acyclic olefin, the total number of linear polymer chains increases by one. The total number of polymer chains is equal to the total number of initial chains ($[C]_o$) plus the total number of chains produced by a chain transfer reaction to acyclic olefin ($[CTA]_o$ - $[CTA]_t$). Therefore, in a ROMP/CT system the $\overline{X_n}$ can be defined as

$$\overline{X_n} = \frac{[M]_o - [M]_t}{([CTA]_o - [CTA]_t) + ([C]_o - [C]_t)}. \quad (3)$$

If the catalyst concentration is chosen such that $[CTA]_o >> [C]_o$, then in the limit of complete conversion of both the M and the CTA, eq 3 reduces to

$$\overline{X_n} = \frac{[M]_o}{[CTA]_o}. \quad (4)$$

The expression for $\overline{X_n}$ given in eq 4 is similar to that for a polymerization of an epoxide initiated by an metal alkoxide or hydroxide in the presence of protic substances such as alcohols.[39] The exchange reaction of a propagating alkoxide with a monomeric alcohol results in the formation of a polymeric alcohol and a monomeric alkoxide that can reinitiate polymerization. The polymeric alcohol is not dead but dormant, and it can participate in an exchange reaction with another propagating alkoxide. In this case each alcohol molecule contributes equally with an initiator species in determining the total number of polymer chains. The $\overline{X_n}$ in this type of polymerization is given by

$$\overline{X_n} = \frac{[M]_o - [M]_t}{[I]_o + [ROH]_o}, \quad (5)$$

where I is the initator (metal alkoxide) and ROH is the monomeric alcohol. In an ideal ROMP/CT system there is no termination of the active species, the catalyst concentration is much smaller than the concentration of CTA, the monomer is completely converted to polymer, and all of the CTA is

incorporated into a polymer chain. If these conditions are met, eq 4 should be valid.

Theoretical Functionality in an Equilibrium ROMP/CT System. The number average functionality $\overline{F_n}$ of a telechelic polymer is defined as the number of functional groups per polymer chain. In the synthesis of telechelics by ROMP/CT the number of functional groups that are incorporated into a polymer chain is ideally equal to two times the number of chain transfer molecules reacted since each CTA contains two functional groups. The total number of polymer chains is equal to the total number of initiators as defined above. This includes the initial catalyst that reacted and initiators that are formed by reaction with the chain transfer agent. The only chain ends that do not contain a fragment from the chain transfer agent are those from the initial catalyst and those from any termination reaction. An expression for the theoretical functionality in a ROMP/CT system is given in eq 6

$$\overline{F_n} = \frac{2([CTA]_o - [CTA]_t)}{([CTA]_o - [CTA]_t) + ([C]_o - [C]_t)}. \qquad (6)$$

In the limit of 100% conversion of the CTA and complete initiation of the catalyst eq 6 reduces to

$$\overline{F_n} = \frac{2[CTA]_o}{[CTA]_o + [C]_o}. \qquad (7)$$

It is convenient to define r as the ratio of $[CTA]_o$ to $[C]_o$. This ratio is the relative number of functionalized endgroups to nonfunctionalized

endgroups where a nonfunctionalized endgroup is any endgroup that does not come from the CTA. The $\overline{F_n}$ as a function of r is given in eq 8

$$\overline{F_n} = \frac{2r}{r+1}. \tag{8}$$

Table 1 shows a number of calculated $\overline{F_n}$'s at different values of r.

Table 1. Theoretical Functionalities Calculated by Equation 8

$r = [CTA]_o/[C]_o$	$\overline{F_n}$ (from eq 8)
1	1.000
10	1.818
100	1.980
500	1.996
1000	1.998

It is clear from Table 1 that for functionalities that are very close to 2.0, a r value of at least 100 must be used (when $[CTA]_o >> [C]_o$ eq 8 reduces to $\overline{F_n}$ = 2.0). Again, this is in the limit of 100% conversion of the CTA. At 50% conversion the effective r is reduced by one-half (eq 6).

As the target molecular weight (from the preceeding section, $\overline{X_n} \approx [M]_o/[CTA]_o$) becomes larger, the negative contribution to the $\overline{F_n}$ by the catalyst becomes more severe. That is, r becomes smaller if the $[M]_o/[C]_o$ ratio remains constant. In order to achieve $\overline{F_n}$ which are very close to 2.0, r must

be kept > 100 ($\overline{F_n}$ > 1.98), and therefore the $[M]_o/[C]_o$ ratio must be adjusted accordingly at different $[M]_o/[CTA]_o$ ratios. For example, if the target $\overline{X_n}$ is 10 and the desired functionality is > 1.98, then the $[M]_o/[CTA]_o$ ratio should be ≈ 10 and r should be > 100. This leads to a $[M]_o/[C]_o$ ratio of 2000 (at r = 200). Optimized (r = 200) $[M]_o/[C]_o$ ratios at various $[M]_o/[CTA]_o$ ratios are calculated in Table 2.

Table 2. Calculated $[M]_o/[C]_o$ Ratios for Number Average Functionalities >1.98 (r = 200) at Different Degrees of Polymerization

$\overline{X_n}$ ($[M]_o/[CTA]_o$)	$[M]_o/[C]_o$
2	400
5	1000
10	2000
25	5000
50	10000

There are no viable mechanisms in this type of ROMP/CT system that would result in a $\overline{F_n}$ value greater than 2.0. However, there are two consequences of a ROMP/CT which would negatively effect the $\overline{F_n}$. The first is the contribution of the initiating carbene and the endgroup derived from termination processes. The second is the contribution of large cyclic oligomers in the polymer sample. Cyclic oligomers that are not removed from the polymer sample during purification (e.g. precipitation) will contribute to the

total number of "chains" but do not have any endgroups. Therefore, large cyclic oligomers will negatively effect the $\overline{F_n}$ (eq 7). Low molecular weight cyclics are typically removed from the polymer by precipitation in an appropriate nonsolvent for the polymer. Cyclics lower the $\overline{F_n}$ for a given telechelic, but they are not as detrimental in a step condensation polymerization as a monofunctional telechelic. This is because they are *nonfunctional* and do not participate in a step polymerization. Therefore, if the $\overline{F_n}$ is low, the concentration of the telechelic can be simply be increased. This increases the concentration of cyclics, but they do not contribute to a stoichiometric imbalance.

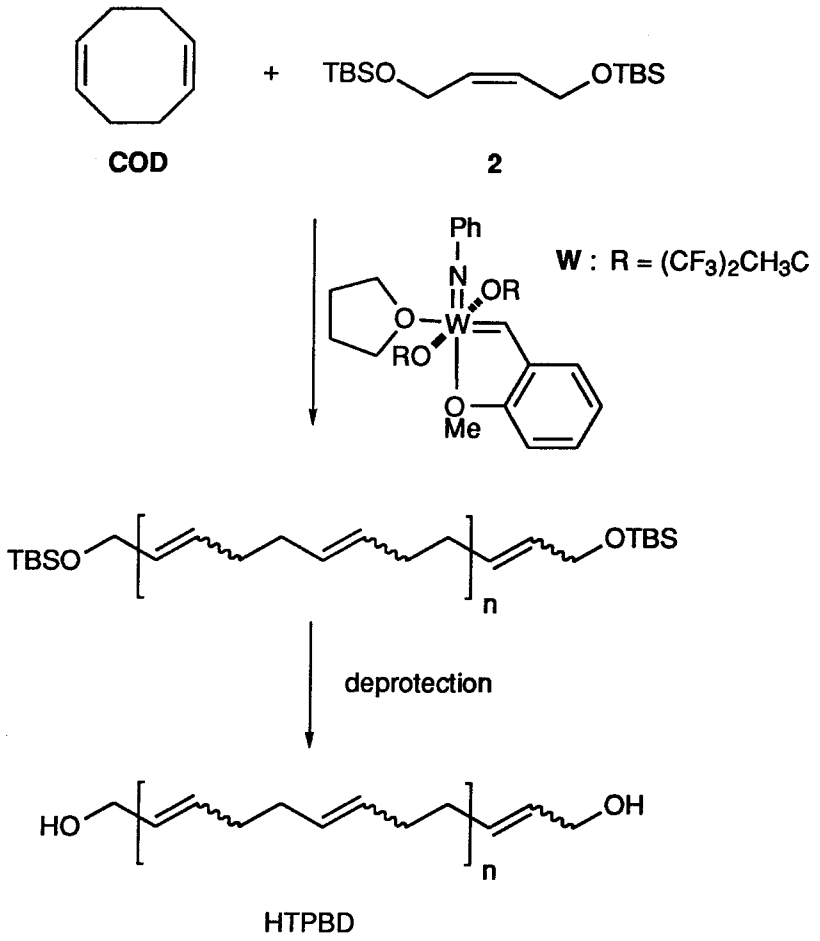
From the above analysis molecular weight should be controlled by the $[M]_o/[CTA]_o$ ratio, and the $\overline{F_n}$ should be controlled by the $[CTA]_o/[C]_o$ ratio. In this chapter the use of unicomponent, well-defined metathesis catalysts of high activity for the preparation of telechelic polymers will be discussed. The focus of the discussion will be on the preparation of HTPBD.

Results Employing Metathesis Catalysts Based on Tungsten and Molybdenum

Initial Investigations. The following data are results on the preparation of HTPBD using a protected allylic diol as the chain transfer reagent and a single component metathesis catalyst with a well-defined initiating alkylidene. The ROMP of 1,5-cyclooctadiene (**COD**) leads to a polymer having a repeat unit that is identical to that of 1,4-polybutadiene. The ROMP of **COD** in the presence of a difunctional acyclic olefin should result in a telechelic polymer that is formally telechelic 1,4-polybutadiene.

The catalyst chosen for the initial chain transfer reactions was W(CHAr)(NPh)[OCMe(CF3)2]2(THF) (Ar = *o*-methoxyphenyl) (**W**), due to its ease of synthesis and high metathesis activity.[35,41] The readily available *cis*-2-butene-1,4-diol (**1**) was protected as the bis-*tert*-butyldimethylsilyl (TBS) ether (**2**)[42] which was used as the CTA. The reaction is outlined in Scheme 3. Protection of alcohols in this molecule is necessary due to the extreme sensitivity of **W** toward protic functionality.[43] In a typical experiment, **COD** and **2** were mixed in a vial under an inert atmosphere and transferred by syringe to a separate vial that contained **W** (dissolved in a minimum amount of benzene). The reactions were performed in a minimum amount of solvent in an effort to keep the relative concentration of cyclic oligomers to a minimum.[18] The molar ratio of **COD** to **2** was varied from 54 to 654, and the mol ratio of COD to **W** was kept constant at 700. All reactions were run at room temperature for two hours and terminated by the addition of excess pivalaldehyde. The active catalyst should react in a Wittig-type reaction with the aldehyde to give the corresponding metal-oxo species and an olefin.[37,44]

Scheme 3



The reaction mixtures were then dissolved in benzene and the polymer was precipitated by the additon of methanol. The results are shown in Table 3. The molecular weights of the polymers decreased with increasing concentration of chain transfer agent. The relationship between $\overline{X_n}$ and the $[COD]_o/[2]_o$ ratio is shown in Figure 1. The relationship in Figure 1 is linear for entries 3-6, however significant deviation is seen for entry 2. Also there is a dramatic decrease in the yield of isolated polymer with an increase in the

Table 3. Results From ROMP/CT System Employing COD, 2 and W

entry	$[COD]_o/[2]_o$	$[COD]_o/[W]_o$	$10^{-3}\overline{M_n}^a$	PDI[a]	yield (%)
1	∞	712	47.4	2.1	92
2	654	710	41.7	2.0	90
3	182	713	37.1	2.0	71
4	107	708	26.9	2.1	62
5	79	701	21.3	2.1	51
6	54	713	14.1	3.0	40

[a] Determined by GPC in methylene chloride vs. polystyrene standards

amount of **2** present in the polymerization mixture. All efforts to produce a low-molecular-weight polymer using **2** as the CTA (i.e. at $[COD]_o/[2]_o$ ratios <75) resulted in low isolated (<50%) yield of polymer. In general, extended reaction times did not increase polymer yields. For these low yielding polymerizations both unreacted **COD** and unreacted **2** where observed in the methanol fraction.

Although the reaction parameters were not optimized at this stage, low-molecular-weight polymers were deprotected and characterized. To remove the TBS endgroups from a protected polymer, a THF solution of a low-molecular-weight TBS endcapped polymer was reacted with excess tetrabutylammonium fluoride (TBAF) at room temperature for 12 hours. The polymer was precipitated by the addition of methanol, redissolved in

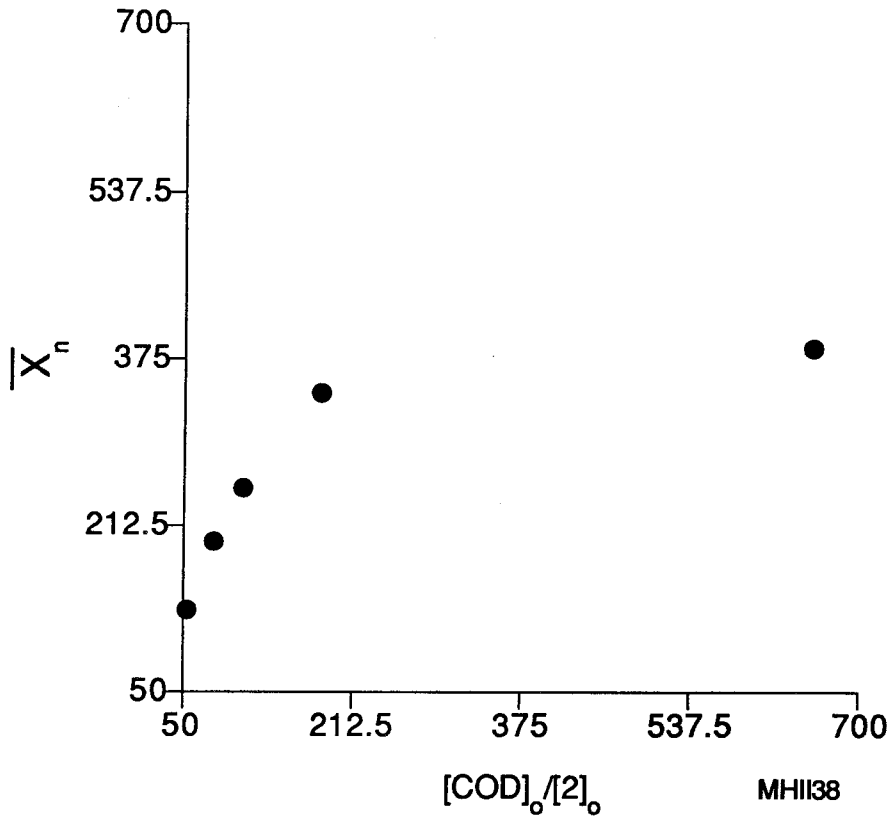


Figure 1. The relationship between $\overline{X_n}$ and $[COD]_o/[2]_o$ for the polymerizations shown in Table 3.

benzene, and filtered twice through silica gel.[45] In order to ensure that the spectrum was not a mixture of polymer and low-molecular-weight impurities (e.g. catalyst residue or **1**), the polymer was further purified by preparatory GPC. Isolation of only the polymeric fraction of this HTPBD was accomplished. Inspection of the ^{1}H NMR spectrum of this rigorously purified sample was virtually identical to the spectrum before this purification step. A representative ^{1}H NMR spectrum of a purified HTPBD polymer is shown in Figure 2. Only signals from the polymer backbone and endgroups are present. The polybutadiene consists of 1,4 repeat units and is high cis (cis olefinic protons are upfield of trans olefinic protons and cis allylic protons are downfield of trans allylic protons). The polymer was found to be 93% cis by ^{13}C NMR spectroscopy. The pseudo-triplets at δ 4.14 and δ 4.04 are assigned to the methylene protons adjacent to the oxygen (both cis and trans isomers) of the endgroup. Addition of trifluoroacetic anhydride to the NMR sample results in the formation of the trifluoroacetate endgroups, the downfield shift of the methylene signals by ~0.75 ppm, and collapse of the pseudo-triplets into doublets. Endgroups from the initiating alkylidene were identified by the presence of singlets at δ 3.81 and δ 3.83. These signals were assigned to the aromatic methoxy group from the initiating alkylidene (both cis and trans isomers) and are seen in the spectra of both the protected and deprotected polymers.[46] The endgroups from the endcapping reagent, pivalaldehyde, were not observed. The ^{1}H NMR spectrum is consistent with 1,4-HTPBD.

Number average functionality $\overline{F_n}$ for the HTPBDs was calculated from the number average molecular weight $\overline{M_n}$ (GPC) and integration of the ^{1}H NMR spectrum. This calculation generally gave $\overline{F_n}$ values between 1.7 and 1.9 for low-molecular-weight samples (Mn < 15000).[47] Although there is

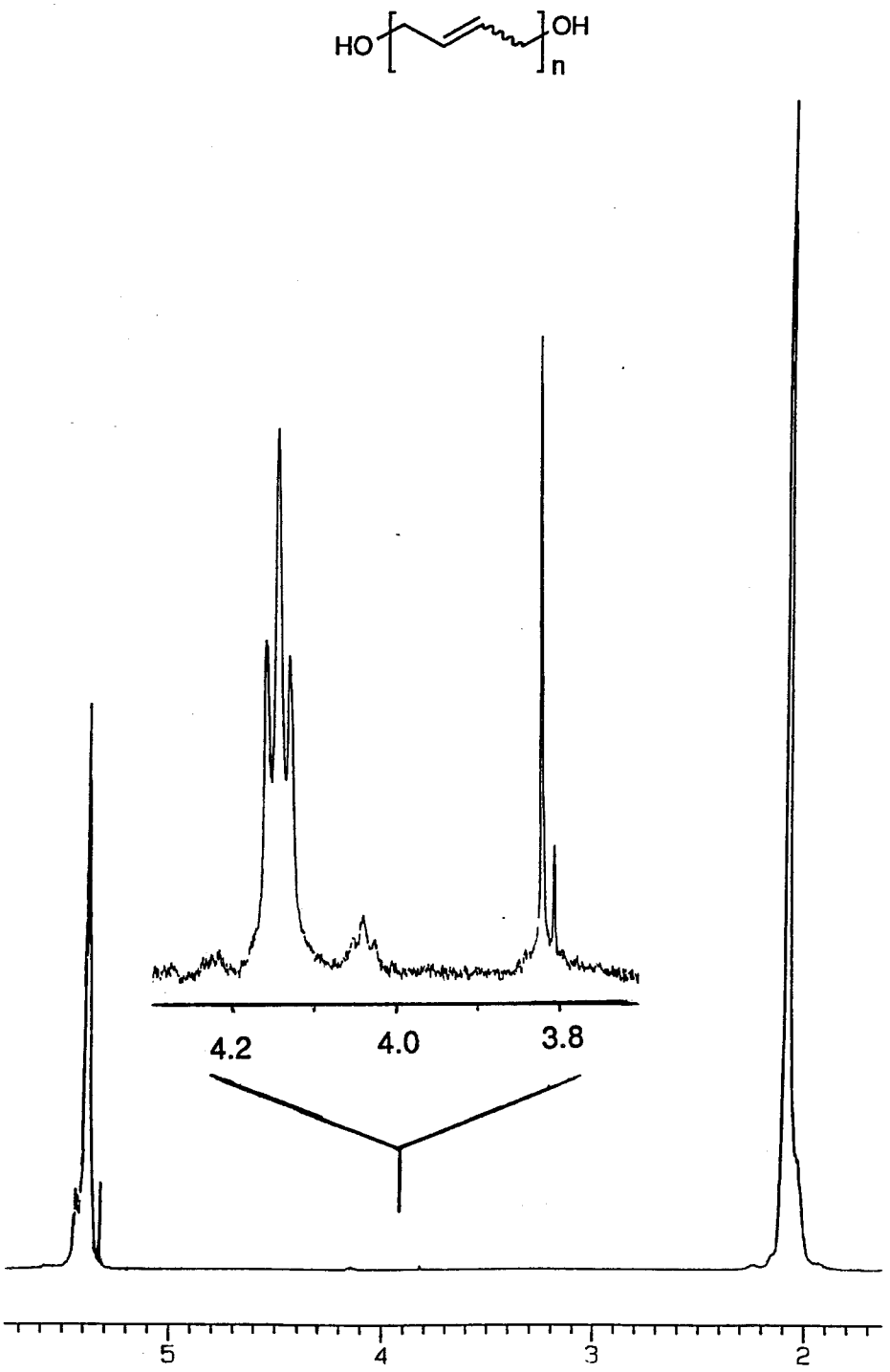


Figure 2. ^1H NMR spectrum (400 MHz, CD_2Cl_2) of a low-molecular-weight ($\overline{M_n}$ = 10.6 x 10^3, CH_2Cl_2 GPC) HTPBD synthesized employing catalyst **W** and CTA **2** (scales are in ppm).

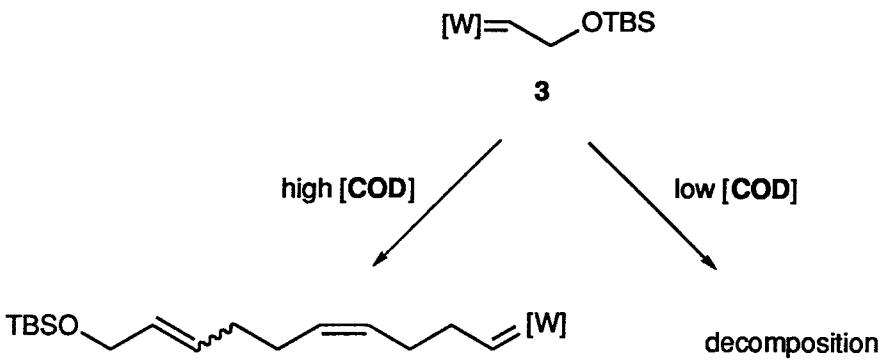
uncertainty in this number, this preliminary calculation of $\overline{F_n}$ was encouraging.

From this initial investigation, it is clear that well-defined HTPBD with one type of regiochemistry (1,4), with one type of reactive endgroup (allylic alcohol), and with a $\overline{F_n}$ close to 2.0 can be synthesized in good to moderate yields by employing a ROMP/CT strategy using a well-defined metathesis catalyst. However, this route (Scheme 3) is not practical for the synthesis of polymers with $\overline{M_n}$ values below 1.0×10^4 due to the significant decrease in yield with increasing concentration of **2**. The nature of this problem is addressed below.

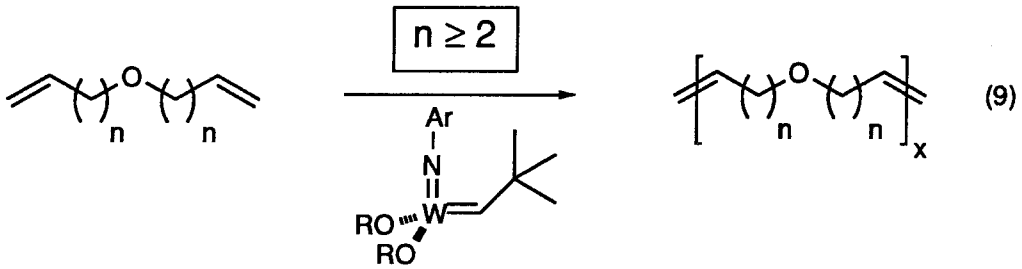
Modification of the Initial CTA (2). In addition to the low yields obtained at relatively low $[COD]_o/[2]_o$ ratios, the presence of endgroup fragments only from the initiating alkylidene and **2** but not from the endcapping reagent suggests that the catalyst decomposes during the course of the reaction. The stability of the alkylidene moiety **3** generated from the reaction of the propagating alkylidene (or initiating alkylidene) with **2** is suspect. It is speculated that in the presence of high **COD** concentrations this alkylidene (**3**) will reinitiate the polymerization, but as the concentration of **COD** decreases during the polymerization an alternative decomposition pathway involving the β oxygen becomes competitive (Scheme 4). Consistent with this is the decrease in the yield of polymerization with increasing concentration of **2** (Table 3) and the insensitivity of the yield to increased reaction time. As a test of this hypothesis the metathesis isomerization of **2** and related derivatives by **W** was investigated.

The proposed instability of **3** is consistent with reported inactivity of tungsten based metathesis catalysts with allylic ethers.[48-52] For example,

Scheme 4

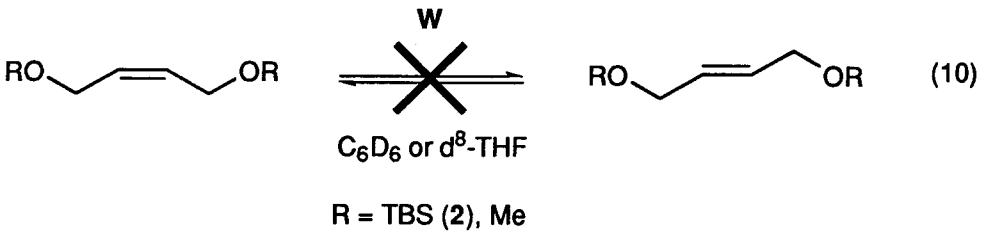


Wagener has shown that a minimum of two methylene groups between the oxygen and the olefin are necessary for sucessful acyclic diene metathesis polymerization (ADMET) of ether containing dienes employing a similar tungsten-based metathesis catalyst (eq 9).[51]



Coordination of the ether to the metal center when n=1 was presumed to deactivate the catalyst. Decomposition of allylic ethers in the presence of the classical metathesis catalyst system $WCl_6/SnMe_4$ to yield a stable tungsten alkoxide complex has also been observed.[50] In light of these results, the metathesis of **2** by **W** was investigated.

Successful metathesis of **2** (>95% cis) should result in the equilibration of the cis/trans isomers of **2** (<95% cis).[18] Metathesis isomerization of **2** and its dimethyl ether analog were attempted in benzene and in THF at substrate to catalyst ratios ranging from 3:1 to 300:1. Isomerization of the double bond was never observed (eq 10).



(10)

Not only was **W** ineffective for the isomerization, but decomposition of the starting carbene species was observed in all cases. Suprisingly, no cross-metathesis of **2** and *cis*-3-hexene or styrene was observed. From these results it is obvious that **2** and related allylic ethers are not compatible with **W**. This is consistent with the previous reports on allylic ether metathesis. However, from the above polymerization results it is clear that the allylic ether fragment is being incorporated into the polymer chain. Therefore, metathesis of carbene **3** with either **COD** or the polybutadiene backbone is occurring. If **2** were only acting as a chain terminating species (i.e. the rate of metathesis of **3** with any other olefin was zero), then a $\overline{F_n}$ close to one would be expected. In analogy to the ADMET polymerization of bisallylic ethers,[51] separation of the oxygen from the olefin by two methylene units should increase the stability of the resultant substituted alkylidene. For the ROMP/CT systems described above, this requires the synthesis of the homoallylic derivative of **2**.

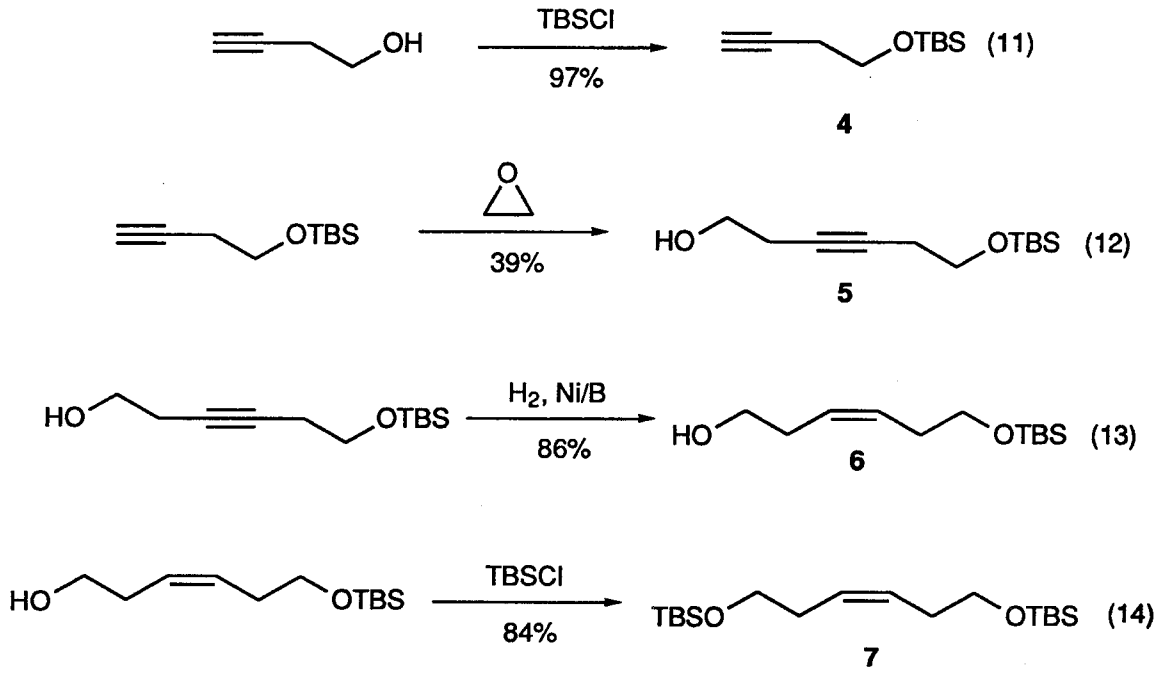
Both cis and trans olefins should be effective CTAs in principle.

However, the use of a cis olefin should increase the realtive rate of CTA incorporation to **COD** polymerization. In fact, in a preliminary experiment using 1,10-bis-*tert*-butyldimethylsiloxy-*trans*-5-decene as the CTA virtually no molecular weight reduction was seen over the same time period used in typical ROMP/CT reactions (2 h). Presumably this is due to the slower reaction of the trans olefin. It is likely, however, that eventual incorporation of this CTA into the polymer would be observed in analogy to the system employed by Chung where a difunctional *trans*-5-decene was employed as a CTA.[29] Nevertheless, since **2** was predominantly cis (>95%) direct comparison of the homoallylic analog requires the synthesis of 1,6-bis-*tert*-butyldimethylsiloxy-*cis*-3-hexene (**7**).

The synthesis of **7** is outlined in Scheme 5. Protection of 3-butyne-1-ol as the *t*-butyldimethylsilyl ether[42] gave compound **4** in 97% yield (eq 11). Ring opening of ethylene oxide by the lithium acetylide drived from **4** was accomplished in liquid ammonia to give **5** in 39% yield (eq 12).[53] Other reaction conditions were investigated (e.g. Lewis acid catalyzed ring opening in THF[54,55]), however the reaction in liquid ammonia gave the highest yields (~40%) and the best reproducibility. Hydrogenation of **5** using the nickel/sodium borohydride based catalyst described by Brown[56] was employed for the semi reduction of the alkyne to give the corresponding cis (>95% cis by NMR and GC) alkene **6** (eq 13). Protection of **6** as the *t*-butyldimethylsilyl ether[42] gave **7** in 84% yield (eq 14). The overall yield for the four steps was 27%, and all of the steps were carried out on a multigram scale.

Isomerization of **7** from >95% cis to ~75% trans by **W** in C_6D_6 at relatively low olefin to catalyst ratios (<10) was observed. Unlike the attempted isomerization of **2**, the initial carbene species from **W** was stable for

Scheme 5



up to 3 months in the presence of **7**. Therefore, the use of **7** as a CTA in the polymerization of **COD** should generally lead to higher yields of polymer compared to **2** at similar $[COD]_o/[CTA]_o$ ratios. A comparison of the two CTAs is shown in Table 4.

Table 4. Comparison of 2 and 7 as CTAs

CTA	$[COD]_o/[CTA]_o$	$[CTA]_o/[W]_o$	$10^{-3}\overline{M_n}^a$	PDI[a]	yield (%)
2	54	13.5	14.1	3.0	40
2	57	10.5	10.7	2.8	51
7	64	11.9	7.2	2.7	98
7	26	24.6	2.8	2.5	92

[a] Determined by GPC in methylene chloride vs. polystyrene standards

These results show that **7** is a much more effective chain transfer agent in terms of molecular weight reduction and polymerization yield. Even at more than twice the concentration of CTA relative to **W**, the homologated CTA gave a much higher yield of polymer. In addition, much lower molecular weights can be synthesized in more reasonable yields using **7** as the CTA. At this point it was clear that **7** was the CTA of choice in these polymerizations even though its synthesis is considerably longer.

The ROMP/CT reactions shown in Table 3 were repeated using **7** as the CTA at significantly lower $[\mathbf{COD}]_o/[CTA]_o$ ratios (11-94 vs. 54-654). Similar reaction conditions were employed however toluene was used as a solvent (the concentration of **COD** in these polymerizations was ~ 5 M). The results are given in Table 5.

Table 5. ROMP/CT Employing 7 as the CTA and W as the Catalyst

entry	$[COD]_o/[7]_o$	$[COD]_o/[W]_o$	$\overline{M_n}^a$	$10^{-3}\overline{M_n}^b$	PDI[b]	yield (%)
1	94	848	7990	14.5	2.3	94
2	37	843	4210	7.4	2.2	96
3	22	841	3490	5.0	2.2	94
4	11	859	2310	3.6	1.9	83

[a] Determined by VPO

[b] Determined by GPC in toluene vs. polystyrene standards

No unreacted **COD** in the methanol washings was observed by gas chromatography (GC). However, unreacted **7** was observed and quantified.

The theoretical $\overline{X_n}$ was calculated using $[7]_o - [7]_t$ as the total amount of CTA incorporated (eq 6 and eq 7). The relationship between the two measured values of $\overline{X_n}$ and $[COD]_o/([7]_o - [7]_t)$ is shown in Figure 3. It is apparent from Figure 3 that there is a linear relationship between the $[COD]_o/[7]_o$ ratio and the observed $\overline{X_n}$. The $\overline{X_n}$ values derived from the VPO measurements were always lower than the $\overline{X_n}$ values derived from the GPC molecular weights. Assuming the VPO molecular weights are more accurate than the GPC molecular weights, $\overline{F_n}$ values for the four samples were calculated from the VPO $\overline{X_n}$ and the ^1H NMR integrations to be 1.3(6), 1.5(4), 1.9(2), and 1.8(6) for entries 1-4 respectively. The $\overline{F_n}$ values calculated for the two higher-molecular-weight samples were disappointingly low. However, for the lower-molecular-weight, samples the functionalities were close to 2.0. The diminished $\overline{F_n}$ values can be attributed to large macrocycles and to unfunctionalized endgroups derived from the catalyst (the calculated theoretical $\overline{F_n}$ values from eq 8 were 1.76, 1.90, 1.92, and 1.96 for entries 1-4 in Table 5 respectively). However, there is inherent error in both the VPO molecular weights[57] and the NMR integrations.[58] The estimated error in the $\overline{F_n}$ values is ± 0.2 assuming ± 15% error in the molecular weight measurement and a ± 5% error in the NMR integration.

In general, significantly higher yields were observed in all cases using **7** as the CTA. The HTPBDs prepared using **7** as the CTA were characterized. Deprotection of the HTPBD was accomplished with TBAF as described in the previous example. Figure 4 shows the ^1H NMR spectrum of a representative low-molecular-weight HTPBD synthesized using **7** as the CTA. As in the initial HTPBDs synthesized only 1,4 repeat units were observed. The multiplet at δ 3.58 was assigned to the methylene protons adjacent to the

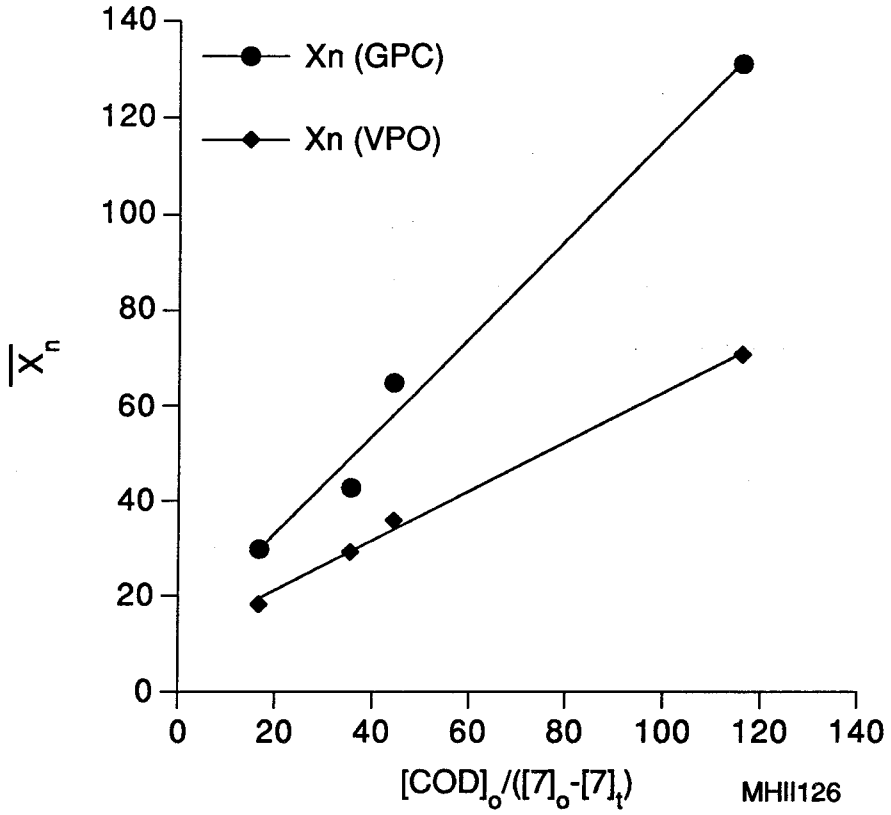


Figure 3. The relationship between $[COD]_o/[7]_o-[7]_t$ and $\overline{X_n}$ from the results in Table 5.

Figure 4. The ^1H NMR spectrum (300MHz, $CDCl_3$) of a HTPBD synthesized employing catalyst **W** and CTA **7** (scale is in ppm).

oxygen for both cis and trans endgroups. Allylic endgroup protons were observed slightly downfield (~δ 2.25) of the backbone allylic protons, and olefinic endgroup protons were observed slightly downfield (~δ 5.5) of the backbone allylic protons. Addition of trifluoroacetic anhydride to this sample resulted in the formation of the trifluoroacetate endcapped polymer. The methylene protons adjacent to the oxygen shifted downfield by ~0.75 ppm, the allylic endgroup protons shifted downfield by ~0.2 ppm, and the olefinic endgroup protons shifted downfield by ~0.1 ppm. The ^{13}C NMR spectrum was also consistent with the structure shown in Figure 4. Two equally intense resonances were observed at δ 62.3 and δ 62.7 and assigned to endgroup carbons adjacent to the oxygen (both cis and trans endgroups). Also, the backbone was determined to be 53% trans from the ^{13}C NMR spectrum. Olefinic and allylic carbons adjacent to the endgroup oxygen were also observed in the ^{13}C NMR spectrum (see experimental for the complete assignment).

Changing the CTA from **2** to **7** resulted in significant increases in the yields of polymer isolated from these ROMP/CT reactions. Lower molecular weight polymers ($<1.0 \times 10^4$) were synthesized and isolated in good yields. The HTPBDs isolated contained only 1,4 repeat units and low-molecular-weight polymers had $\overline{F_n}$ values close to 2.0. This is similar to the results obtained using **2** as the CTA. The endgroups on the HTPBD using **7** as the CTA are homoallylic rather than allylic alcohols. Although the synthesis of **7** is more complicated than the synthesis of **2**, it is a superior CTA for the preparation of HTPBD. However, inspection of Table 5 reveals that the yield of polymer drops off at relatively low $[COD]_o/[7]_o$ concentrations (entry 4). Although this diminished yield is not as severe with **2** as the CTA, the source of this low

yield was investigated by following the progress of a typical ROMP/CT reaction using **7** as the CTA.

Kinetics of Polymerization and Chain Transfer Using 7 as the CTA. In general, the yields of polymerization were much higher using **7** as the CTA, however a decrease in the yield of polymerization was observed at low $[\mathbf{COD}]_0/[\mathbf{7}]_0$ ratios (Table 5, entry 4). Although this decrease was less signifcant than when **2** is used as the CTA, the origin of this low yield was investigated by following the conversion of monomer and CTA in one of these polymerizations using GC. A ROMP/CT experiment similar to entry 4 in Table 5 ($[\mathbf{COD}]_0/[\mathbf{7}]_0 = 11$) was performed, and aliquots were taken from the polymerization at different times and precipitated into methanol. The precipitated polymer was filtered, and the filtrate was analyzed by GC. After 0.33 h there was no **COD** detected by GC. The disappearance of **7** as a function of reaction time is shown in Figure 5. It appears that the maximum amount of **7** is consumed within the first hour of the reaction. Even after 24 h there is no further decrease in the amount of **7** remaining in the solution. Addition of a second aliquot of **W** (~10 mol% **W** relative to the remaining **7**) resulted in almost complete consumption of **7** (< 5% remaining) and a decrease in the viscosity of the polymerization solution. Also, after 48 h two isomers of the cyclic oligomer cyclododecatriene (CDT) were observed by GC (identified by GC/MS). This cyclic was not observed in the first seven aliquots. From these results it appears that both polymerization and chain transfer are fast. However the catalyst decomposes before complete conversion of **7**. If the catalyst were still active, a steady decrease in **7** should have been observed as well as the formation of cyclic oligomers. Moreover, the catalyst appears to have completely decomposed within the first hour of the reaction. Significant

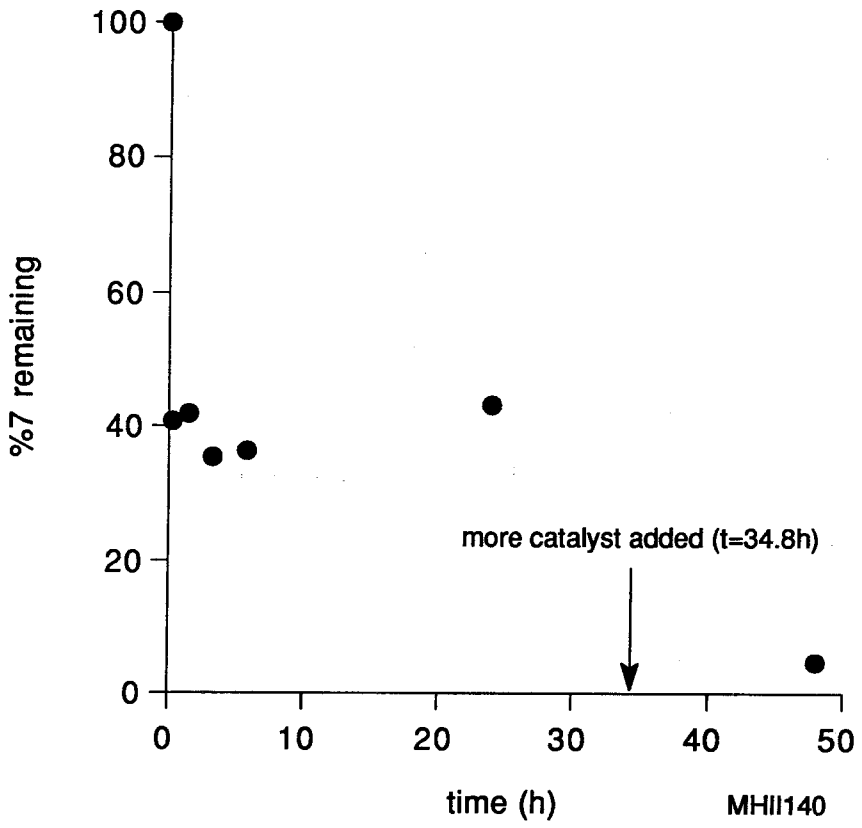
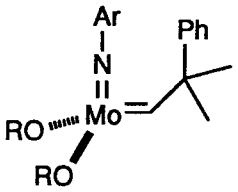


Figure 5. The disappearance of **7** over time in a typical ROMP/CT reaction employing **W** as the catalyst and **COD** as the monomer.

improvements in the yield and monomer conversion are achieved using **7** as the CTA as compared to the the initial systems using **2** as the CTA, but there still exists a problem with catalyst decomposition. Although **W** is readily available and easily synthesized, premature decomposition in the ROMP/CT reactions described above detracts from its usefulness.

In an effort to further increase the yield of polymerization as well as the conversion of CTA, the more robust molybdenum-based metathesis catalyst $Mo(CHMe_2Ph)(NAr)(OCMe(CF_3)_2)_2$ (Ar=2,6-(*i*-Pr)C_6H_3),[59-61] **Mo** was investigated. Complex **Mo** also effected the cis-trans isomerization of **7**, and was employed in a ROMP/CT experiment similar to entry 4 in Table 5 ($[COD]_o/[7]_o = 10$).



Mo: R = $(CF_3)_2CH_3C$
Ar = 2,6-diisopropylphenyl

Again, the progress of the reaction was followed by GC. After 0.5 h no **COD**, ~ 5% of the initial **7**, and CDT were observed. The reaction was followed over 2 days. The results are shown in Figure 6. The amount of CDT was not quantified, however a steady increase in the relative concentration was observed over the first 20 h of the reaction. The concentration of CDT leveled off after 20 h. Larger oligomers were also seen in the GC, but it was not determined if they were linear or cyclic in nature. The residual **7** did not drop below 3% of its original concentration ($[7]_o$) over 2 days.

From the results presented above it is clear that for the most successful ROMP/CT polymerization (in terms of incorporation of CTA and robust

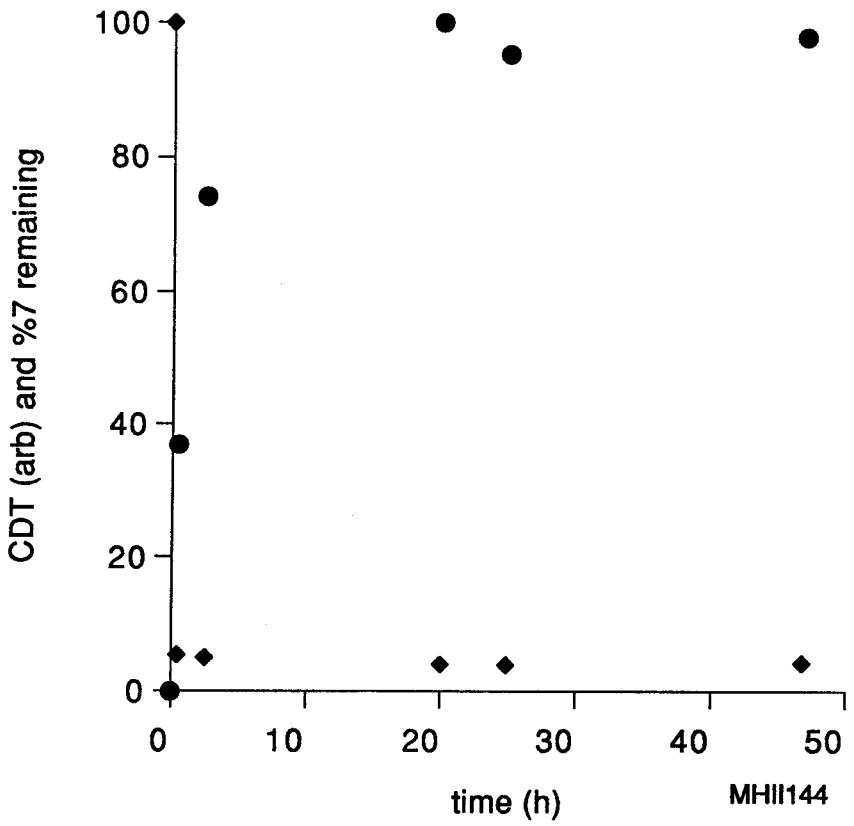


Figure 6. The disappearance of **7** over time (%, ♦) and the appearance of CDT over time (arbitrary units, •) in a typical ROMP/CT employing **Mo** as the catalyst and **COD** as the monomer.

nature of the catalyst) the combination of **7** and **Mo** as the chain transfer agent and catalyst respectively should be employed. The HTPBDs synthesized using **W** or **Mo** as the catalyst were spectroscopically indistinguishable, although the backbone stereochemistry of the HTPBDs synthesisized using **Mo** was generally higher trans. This is consistent with the observed longevity of active species in these polymerizations. In addition, for **Mo** catalyzed polymerizations, significantly higher $[\mathbf{COD}]_o/[C]_o$ ratios could be used without significant decreases in yield. Two polymerizations were performed at $[\mathbf{COD}]_o/[\mathbf{Mo}]_o$ ratios ≈ 1200 and $[\mathbf{COD}]_o/[\mathbf{7}]_o$ ratios of 23 and 80. The yields of isolated polymer were 94 and 98% respectively. As a consequence of the higher $[\mathbf{COD}]_o/[\mathbf{Mo}]_o$ ratios, negative contributions to the $\overline{F_n}$ from the catalyst were minimized. In a subsequent ROMP/CT experiment employing catalyst **Mo** and CTA **7** ($[\mathbf{COD}]_o/[\mathbf{Mo}]_o$=2400 and $[\mathbf{COD}]_o/[\mathbf{7}]_o$=16) a low-molecular-weight HTPBD was synthesized with a $\overline{F_n}$ value of 1.94 (calculated from the VPO molecular weight, $\overline{M_n}$=3250, and ^{1}H NMR integration). A theoretical $\overline{F_n}$ of 1.99 was calculated for this polymerization. Using the increased $[\mathbf{COD}]_o/[\mathbf{Mo}]_o$ ratio, the polymerization mixture contained 83.5% **COD**, 16.3% **7** and 0.2% **Mo** by weight.

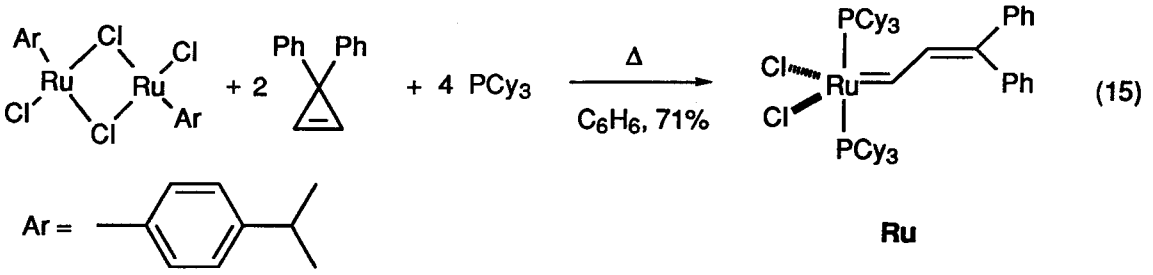
In conclusion, ROMP/CT systems employing well-defined metathesis catalysts based on molybdenum or tungsten are effective for the preparation of endfunctionalized polybutadiene. Protected hydroxyl endgroups were deprotected to give HTPBD. The isolated HTPBDs had one type of alcohol endgroup (allylic, **2**, or homoallylic, **7**) and one type of regiochemistry in the repeat unit (1,4). The HTPBDs produced by **W** were generally higher cis than the polymers produced by **Mo**. The molecular weights of the HTPBDs produced were controlled by the $[\mathbf{COD}]_o/[\mathbf{CTA}]_o$ ratio. $\overline{F_n}$ values close to 2.0

were calculated for low-molecular-weight samples ($\overline{M_n} \leq 4.0 \times 10^3$). For early transition metal catalysts, **7** was a superior CTA compared to **2**. Separation of the oxygen from the metal center by at least two methylene units significantly enhances the longevity of the active species. Also, complex **Mo** outperformed complex **W** in terms of stability. This is in accord with the reported relative stabilities of tungsten and molybdenum-based metathesis catalysts.[21,38,59]

Results Employing a Metathesis Catalyst Based on Ruthenium

Recently a well-defined metathesis catalyst based on ruthenium was synthesized in our laboratory.[62] The complex $Ru(PCy_3)_2Cl_2CHCHCPh_2$ (**Ru**) is effective for the metathesis of acyclic olefins (e.g. *cis*-2-pentene) and low-strain cyclic olefins (e.g. cyclopentene, cyclooctene, **COD**). The catalyst also exhibits significant functional group tolerance as compared to tungsten and molybdenum derived metathesis catalysts. Although the rate of metathesis is somewhat slower using **Ru** as the catalyst in comparison to early transition metal metathesis catalysts, its preferential reactivity with olefins in the presence of polar functional groups is advantageous for the metathesis of functionalized olefins.[62] The utility of this catalyst has been exploited in the both ROMP[63,64] and ring-closing metathesis.[65] Its application to the synthesis of telechelic polymers employing the ROMP/CT strategy described in the preceding section is the subject of this section.

The one-pot synthesis of **Ru** described by Nguyen and Grubbs[66] is shown in eq 15 and was repeated on large scale for the work described below.



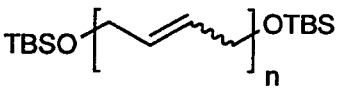
(15)

The ruthenium dichloride cymene dimer was synthesized on large scale following a published procedure.[67] The preparation of 3,3-diphenyl cyclopropene has been simplified and optimized by our group so that it can be

easily synthesized on a multigram scale in high yield.[68] Complex **Ru** is a brick red powder that is stable in the solid state. Storage of the catalyst under an inert atmosphere is recommended, however **Ru** remains active for the polymerization of norbornene and norbornene derivatives after being exposed to air in the solid state for months.

Complex **Ru** was reported to metathesize allyl ether, allyl alcohol, 3-butene-1-ol, and methyl oleate.[62] The metathesis of allylic ethers is relevant to the synthesis of HTPBD. If the metathesis of allylic ethers occurs without complication (e.g. catalyst decomposition), then **2** and related compounds could potentially be used as CTAs in the preparation of HTPBD. As a test both **7** and **2** were employed as CTAs with **Ru**.

In a preliminary experiment it was determined that complex **Ru** is an effective catalyst for a ROMP/CT polymerization employing **COD** and **7** ($[\mathbf{COD}]_o/[\mathbf{7}]_o$=13.4, $[\mathbf{7}]_o/[\mathbf{Ru}]_o$=32.1, $[\mathbf{COD}]_o/[\mathbf{Ru}]_o$=430). A TBS protected HTPBD was obtained in near quantitative yield that was spectroscopically indistinguishable from samples prepared employing CTA **7** and catalyst **W** or catalyst **Mo**. A second ROMP/CT experiment was performed using **2** as the CTA. A $[\mathbf{COD}]_o/[\mathbf{Ru}]_o$ ratio of 3400 and a $[\mathbf{COD}]_o/[\mathbf{2}]_o$ ratio of 17 in toluene ($[\mathbf{COD}]_o \approx$ 5M). The reaction viscosity slowly increased at a polymerization temperature of 40 °C. The reaction was allowed to stir at 40 °C for 19.5 h. The polymer was isolated by precipitation from methanol and isolated in 62% yield. The ^{1}H NMR spectrum of the TBS endcapped HTPBD is shown in Figure 7. From these preliminary experiments it was clear that complex **Ru** is compatible with the ROMP/CT processes described in the above sections. Although the silicon-based protecting group is relatively easy to remove from the polymer endgroups,[69] a more conventional protecting group was



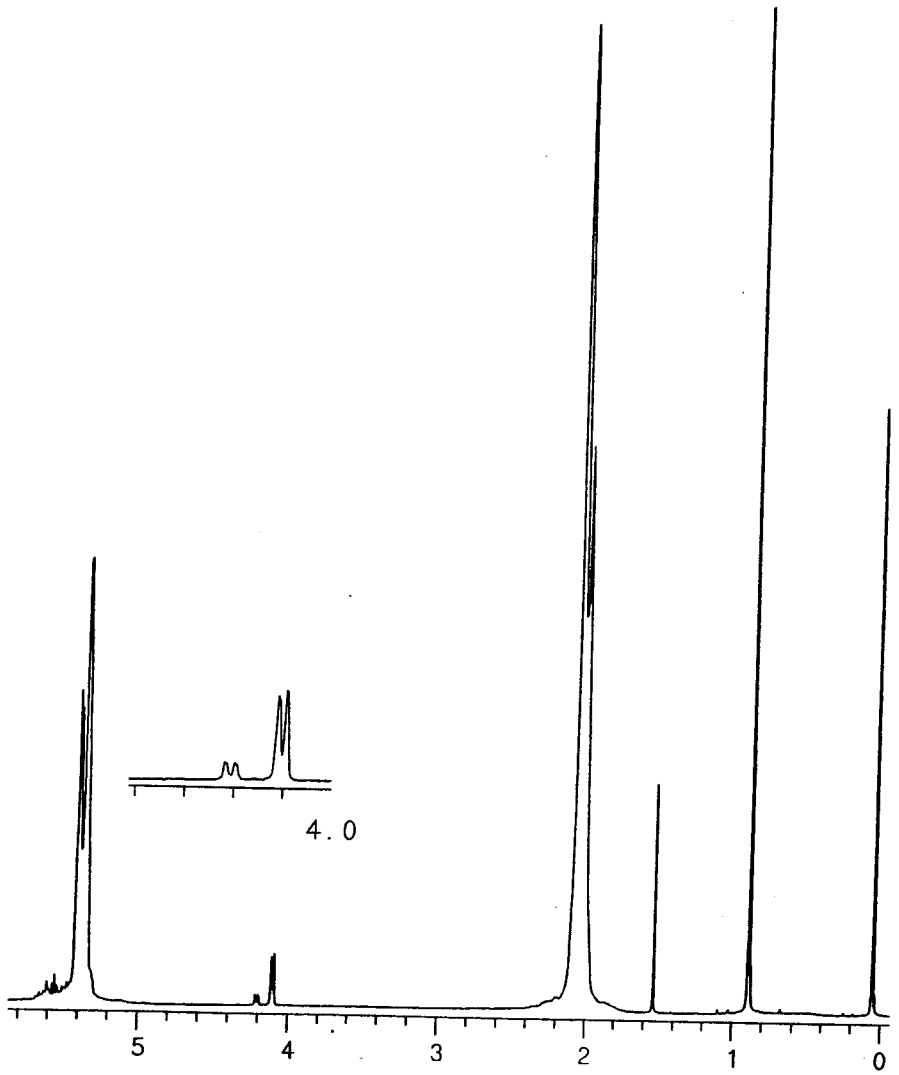
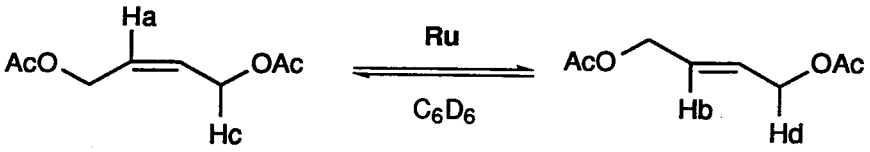


Figure 7. The ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of a TBS protected HTPBD synthesized employing catalyst **Ru** and CTA **2** (scale is in ppm).

investigated. The acetate protecting group is an economical protecting group for alcohols that can be readily removed.[69] 1,4-bis(acetoxy)-*cis*-2-butene (**8**) was synthesized and tested as a CTA.

Synthesis of **8** can be accomplished on large scale via acylation of **1** using acetic anhydride and triethylamine. As a compatibility test, the metathesis isomerization of **8** was investigated. A C_6D_6 solution of **Ru** and **8** (~0.5M, 56 eq) was heated to 45 °C in an NMR tube and the isomerization was monitored by inspection of the allylic methylene proton resonances. The appearance of the trans isomer was followed over time. Two representative ^1H NMR spectra are shown in Figure 8; the first at t=0.1 h and the second at t=15.5 h. After a significant amount of trans isomer had formed another aliquot of **8** was added to decrease the amount of the trans isomer. Subsequent isomerization back to a predominantly trans mixture was observed. The relative amount of trans isomer versus time for this isomerization is plotted in Figure 9. Similar isomerization behavior was observed for the bis(benzyl)ether of **1**. In contrast, complex **Mo** does not effect the isomerization of **8** in C_6D_6 and only decomposition of **Mo** is observed. The ability of **Ru** to repeatedly isomerize **8** suggests that this combination would be effective for the preparation of HTPBD in a ROMP/CT system.

A ROMP/CT experiment was performed using **8** as the CTA and **Ru** as the catalyst on a 20 g scale in toluene ($[\mathbf{COD}]_o/[\mathbf{Ru}]_o \approx 4700$, $[\mathbf{COD}]_o/[\mathbf{8}]_o \approx 30$). No significant exotherm was observed in this polymerization unlike the **Mo** catalyzed polymerization performed at half the scale.[70] The reaction was heated to 45-50 °C for 27 h. A light-yellow, clear oil was isolated in 88% yield by precipitation from methanol.[71] The ^1H NMR spectrum of this oil was consistent with expected acetate endcapped polybutadiene. The acetate



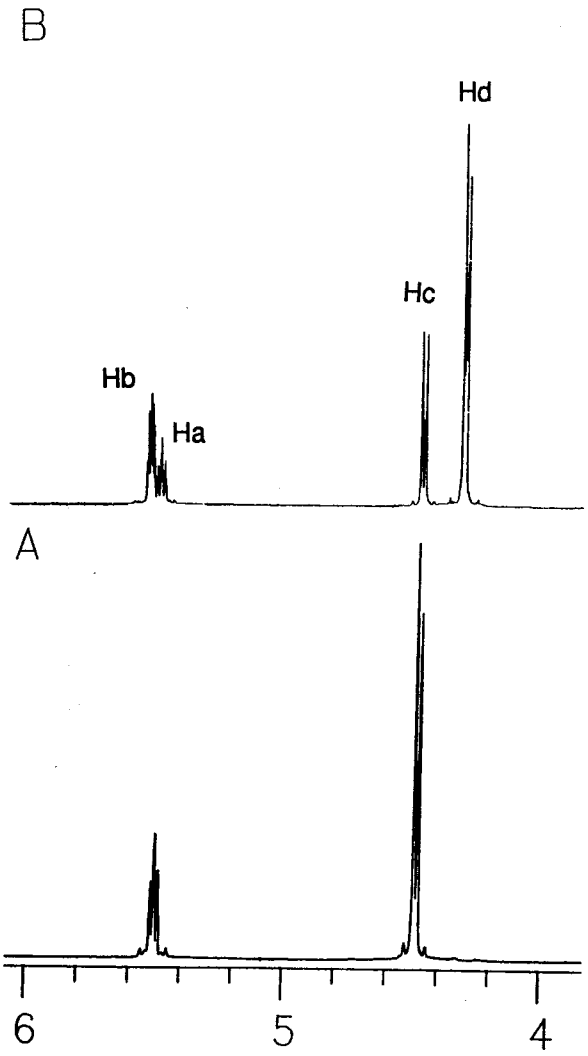


Figure 8. ^{1}H NMR (300 MHz, C_6D_6) spectra monitoring the isomerization of **8** by **Ru** at 45 °C (A, t = 0.1 h; B, t = 15.5 h, scale is in ppm).

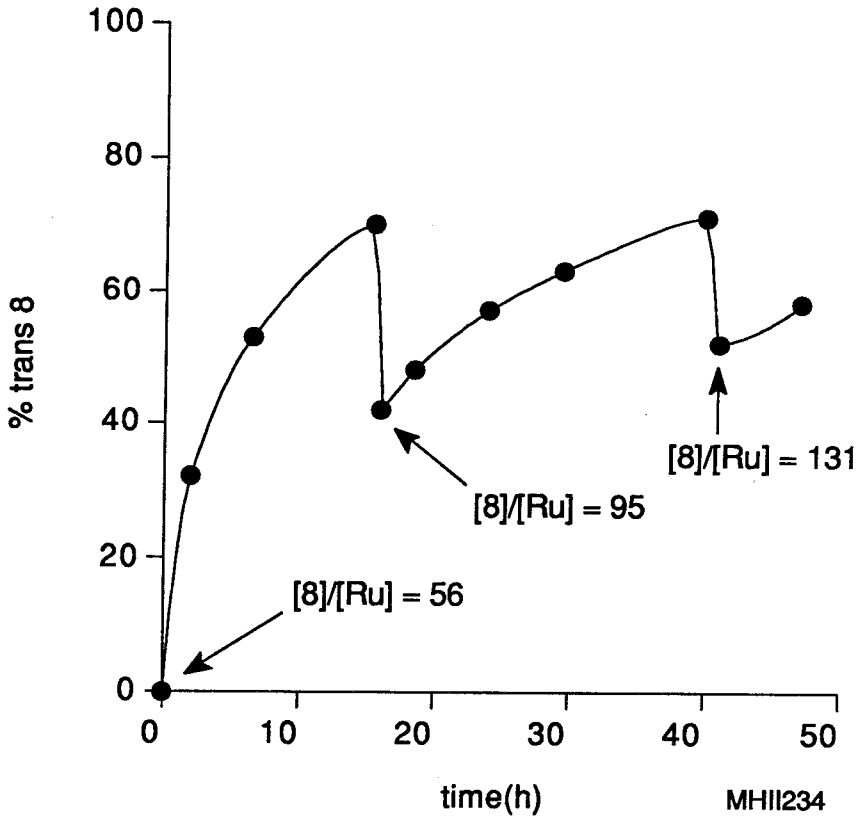
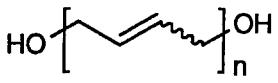


Figure 9. The isomerization of **8** by **Ru** as a function of time. Fresh aliquots of **8** were added t=16 h and t=41 h.

endgroups were removed by treatment of a THF solution of the polymer with 0.7M sodium methoxide in methanol at 0 °C for 6 h. A number of deprotection schemes were investigated,[72] and treatment of the polymer with sodium methoxide (NaOMe) in methanol was found to be the cleanest and most efficient. After deprotection, the polymer was precipitated by the methanol. A colorless clear oil was isolated. The ^{1}H NMR spectrum is shown in Figure 10. The doublets at δ 4.16 and δ 4.06 were assigned to the methylene protons adjacent to oxygen in the polymer endgroups. The muliplet between δ 5.6 and δ 5.7 was assigned to the olefinic endgroup protons. Indeed, addition of trifluoroacetic anhydride to an NMR sample of the HTPBD resulted in a downfield shift of the methylene signals by ~0.75 ppm and the olefinic signals by ~0.3 ppm. Both of these shifted peaks were well-resolved and had similar integration intensities.

Results from representative ROMP/CT experiments employing **8**, **COD**, and **Ru** are shown in Table 6. The polymerizations can be performed in toluene or in the absence of solvent. $[\mathbf{COD}]_o/[\mathbf{Ru}]_o$ ratios close to 5000 can be used without complication (entries 2, 3, and 5). For entries 1, 2, and 3 the $\overline{F_n}$ values were determined by measuring the molecular weight by VPO and the hydroxyl equivalent weight by titration.[73] Of the techniques used to measure functionality in this chapter, this is the most precise and accurate. An error of ±0.1 was estimated for the $\overline{F_n}$ values calculated. Again, the values were close to 2.0.

Aliquots from the polymerization shown in Table 6 entry 5 were precipitated in methanol and analyzed by ^{1}H NMR spectroscopy. The ratio of the endgroup resonances to the backbone resonances gives an estimate of $\overline{X_n}$ according to eq 16



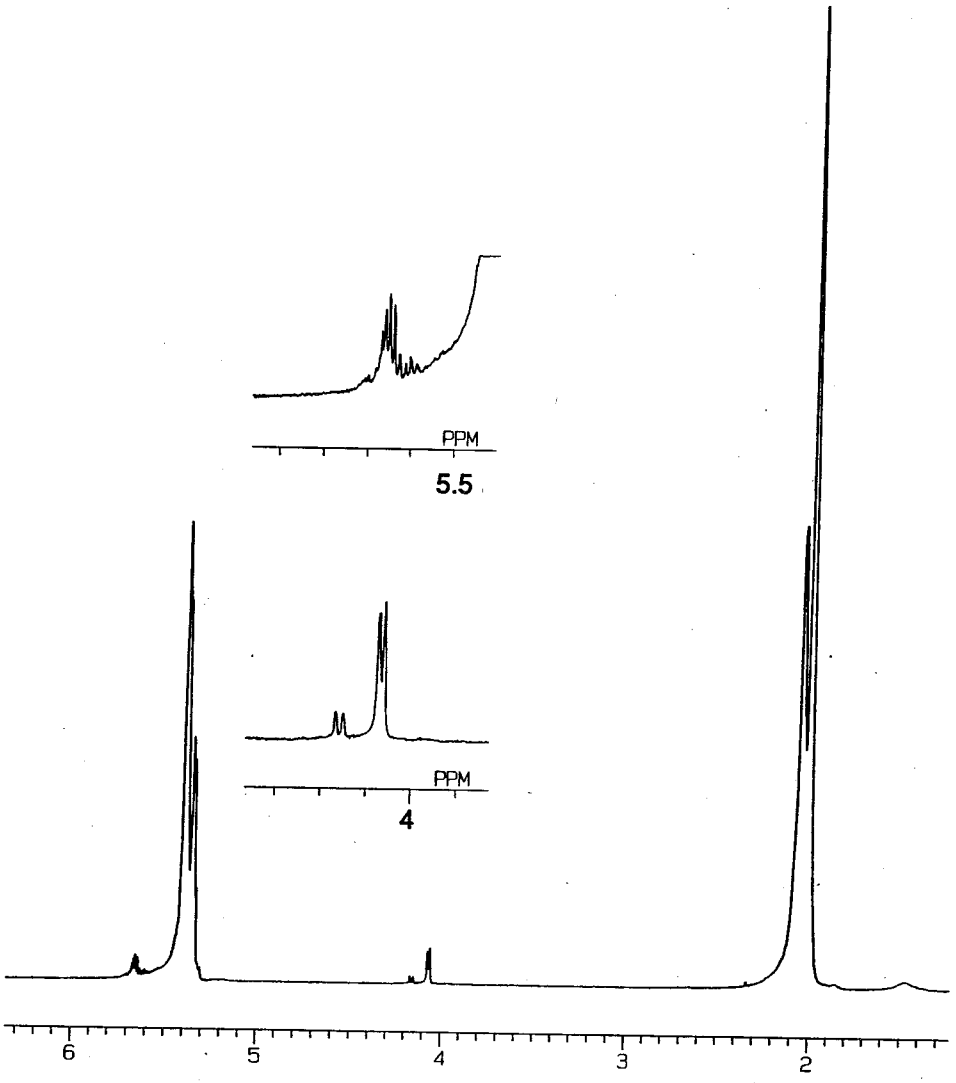


Figure 10. The ^1H NMR spectrum (400 MHz, $CDCl_3$) of HTPBD synthesized employing catalyst **Ru** and CTA 8 (scales are in ppm).

Table 6. Results Employing Catalyst Ru and CTA 8

entry	$[M]_o/[C]_o$	$[M]_o/[CTA]_o$	[M][a]	scale (g)[b]	yield[c]	$10^{-3}\overline{M_n}$[d]	PDI[d]	$\overline{M_n}$[e]	$\overline{F_n}$[f]	%trans[h]	t (h)	T (°C)
1	3000	15	5	25	60	5.0	1.3	2830	1.90	65	16	45
2	4700	44	5	26	80	10.1	1.6	6940	2.05	50	20	45
3	4900	43	neat	135	88	-	-	6430	1.81	40	6	45
4	3700	14	5	115	71	4.3	1.5	2920g	-	60	20	45
5	4600	11	neat	127	88	-	-	2040g	-	45	22	48
6	4700	30	>5	19	88[i]	-	-	4240g	-	60	28	45

[a] As a solution in toluene

[b] Scale = grams COD + grams 8

[c] Isolated yield of deprotected polymer

[d] As determined by GPC in methylene chloride

[e] As determined by VPO

[f] Determined from the VPO $\overline{M_n}$ and the hydroxyl equivalent weight by titration[73]

[g] Determined from the ^1H NMR spectrum assuming $\overline{F_n} = 2.00$

[h] Estimated from the ^1H NMR or ^{13}C NMR spectrum

[i] Calculated before deprotection

$$\overline{X_n} = \left(\frac{I_{ol}}{I_{eg}} \right) \tag{16}$$

where I_{ol} is the area under the resonances for the olefinic protons and I_{eg} is the area under the resonances for the methylene protons adjacent to the acetate endgroups (there are four olefinic protons per repeat unit and there are four methylene protons per a perfectly difunctional chain). The $\overline{X_n}$ as calculated by ^1H NMR is plotted versus time in Figure 11. Inspection of Figure 11 reveals that incorporation of the CTA is still occurring after 11.5 h into the polymerization. In a separate experiment, the progress of a ROMP/CT catalyzed by **Ru** was followed by ^1H NMR spectroscopy. An NMR sample containing a neat polymerization mixture ($[\mathbf{COD}]_o/[\mathbf{Ru}]_o$=1450, $[8]_o/[\mathbf{Ru}]_o$=167, $[\mathbf{COD}]_o/[8]_o$=8.7) was prepared. A capillary tube filled with C_6D_6 and mesitylene as the deuterium lock source and internal standard respectively was added to the NMR sample. The tube was heated to 50 °C in the probe of the NMR spectrometer and the progress of the reaction was followed. Seven resonances were integrated for every spectrum taken thereafter: (1) aromatic protons in mesitylene (standard); (2) methylene protons from cis **8**; (3) methylene protons from cis endgroups; (4) methylene protons from trans **8**; (5) methylene protons from trans endgroups; (6) allylic protons in **COD**; (7) allylic protons in the polymer. Three representative ^1H NMR spectra showing the region containing all of the endgroup and CTA methylene protons from **8** is shown in Figure 12. Three percentages were calculated from the aforementioned integration intensities: the percentage of **COD** incorporated into the polymer, the percentage of **8** incorporated as endgroups, and the percentage of trans repeat units in the polymer. The results are depicted in

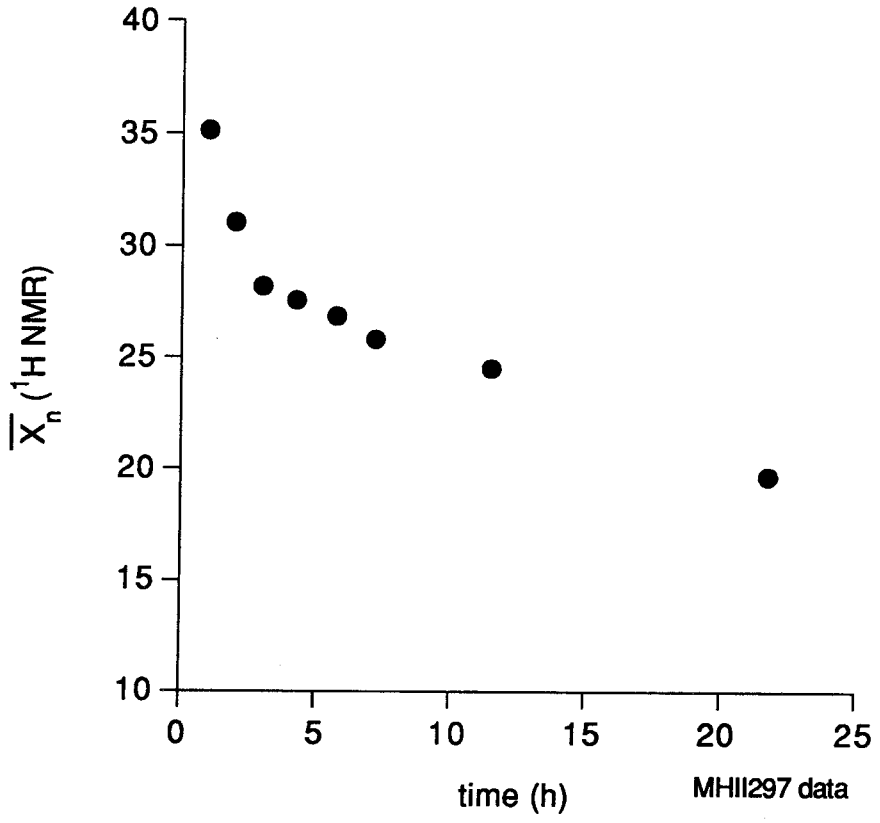


Figure 11. The $\overline{X_n}$ as a function of time for entry 5 in Table 6.

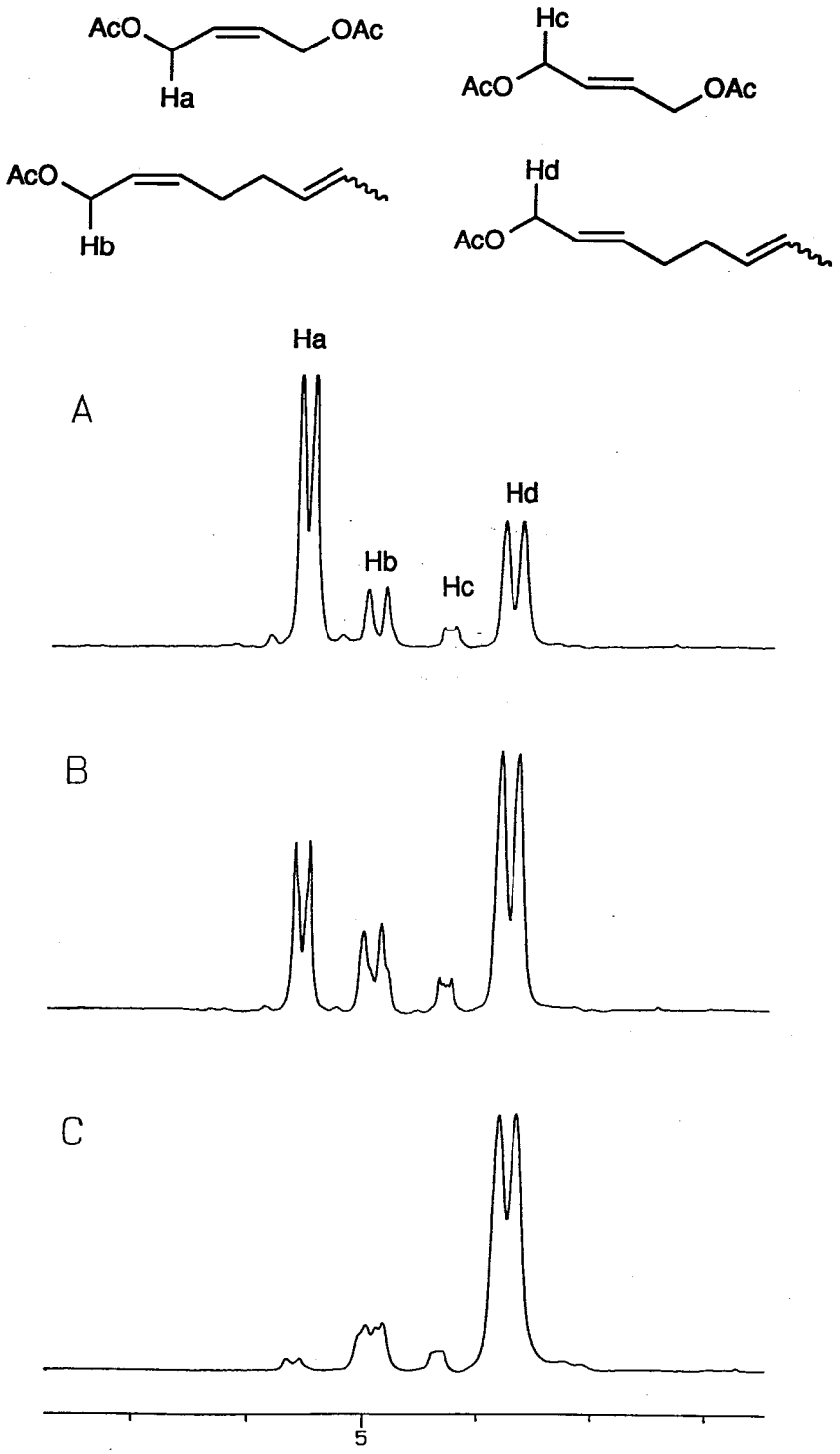


Figure 12. The methylene region of the ^{1}H NMR spectrum of a neat polymerization of **COD** in the presence of **8** by **Ru** (A, t=0.92 h; B, t=2.75 h; C, t=15 h, scale is in ppm).

Figure 13. The sum of the methylene proton resonances from **8** and endgroups and the sum of the allylic protons from **COD** and the polymer were constant (±5%) for all of the spectra taken, indicating that sufficient relaxation was achieved. After 2.75 h at 50 °C ~98% of the **COD** had been polymerized, and ~71% of **8** had been incorporated as endgroups. Over the next 12 hours a steady increase in both the concentration of endgroups and trans repeat units was observed. This indicates that the catalyst is still active for metathesis. An increase in the trans content of a unsaturated polymer in the presence of a metathesis catalysts is a general phenomenon of ROMP.[18] Careful inspection of the resonance due to the cis endgroup (Hb) shows that there seem to be two overlapping signals. This is speculated to be from cc endgroups (endgroup double bond configuration is cis and penultimate doulbe bond is cis) and ct endgroups. This overlapping is seen after most of the **COD** had been consumed. After 15 h at 50 °C ~99% of the **COD** had polymerized, ~89% of **8** had been incorporated as endgroups, and the polymer was ~54% trans.

Catalyst **Ru** is remarkably robust. Although the polymerizations are generally slower employing **Ru**, the ability to use a readily available CTA (**8**), do the polymerization on very large scale,[74] and to use a catalyst that is readily synthesized and extremely tolerant of functional groups makes this type of ROMP/CT system significantly more attractive than the systems presented in the first section of this chapter. In an effort to further enhance the utility of the system, chain transfer agents similar to **8** and **7** with free alcohol groups were investigated.

The reported metathesis of alcohol containing olefins by **Ru**[62] is particularly interesting since the use of a CTA with a free hydroxyl group is

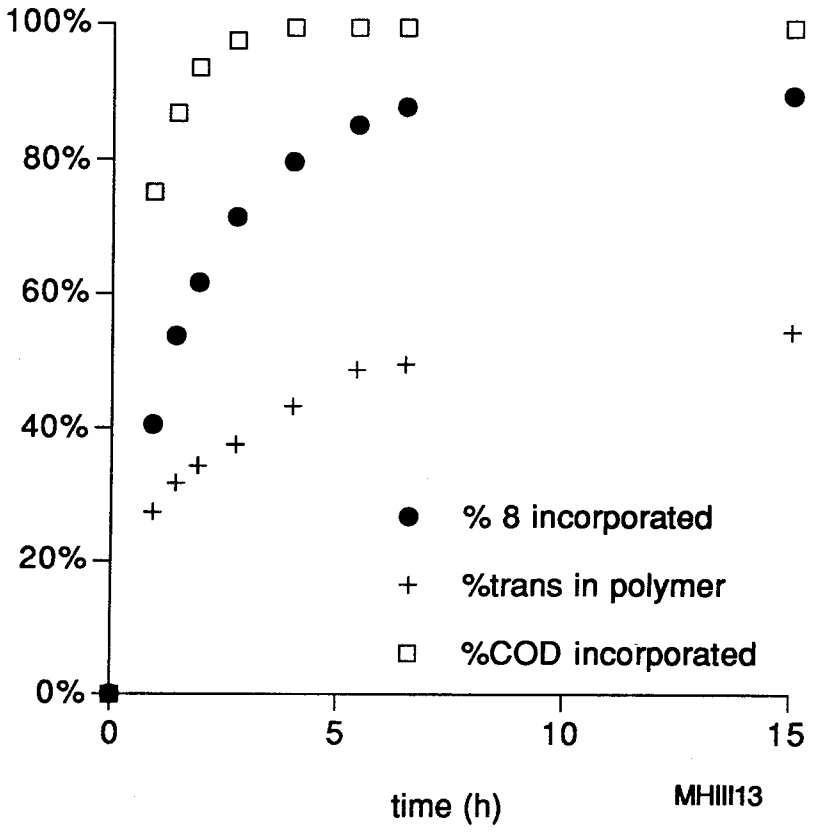


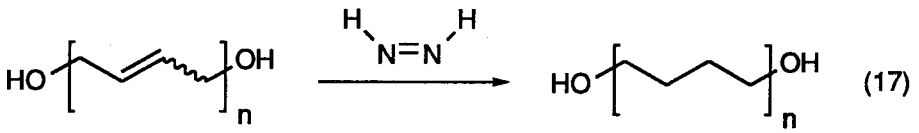
Figure 13. Progress of a ROMP/CT polymerization followed by ^{1}H NMR spectroscopy employing catalyst **Ru** and CTA **8**.

straightforward. In preliminary experiments, two olefinic diols were tested as chain transfer agents. In contrast to scheme 3, the use of an unprotected CTA would obviously eliminate the need to perform a chemical transformation on a polymeric substrate. Both *cis*-2-butene-1,4-diol (**1**) and *cis*-3-hexene-1,6-diol were employed in ROMP/CT polymerizations with **COD** and **Ru**. Generally, both CTAs were effective molecular weight regulating agents, and the isolated polymers contained endgroups derived from the CTAs. However, incorporation of these CTAs was slow, there was incomplete conversion of **COD**, and molecular weight regulation was modest compared to the systems described above using protected CTAs with **Ru**. In the case of **1** the ^{1}H NMR spectrum of the resultant polymer was significantly more complicated than for any previously synthesized HTPBD. Notably, there were resonances assigned to aldehyde groups. This is consistent olefin isomerization (presumably from a metal hydride species) to afford the corresponding enols, which has been observed by Nguyen and Grubbs.[75]

The HTPBDs syntheisized by the method employing catalyst **Ru**, CTA **8** and **COD** are currently being investigated as substitutes for currently available HTPBDs. There has been particular interest in the use of the ROMP/CT HTPBDs in the preparation of polyurethanes used as rocket propellent binders. Preliminary results suggest that these polyurethanes have improved mechanical properties compared to polyurethanes prepared with currently available HTPBDs.[76]

Preparation of Hydroxytelechelic Polyethylene. The hydrogenation of polymers increases their thermal and oxidative stabilities relative to their unsaturated counterparts.[77,78] Telechelic polyethylenes can be synthesized by radical methods[2] or by hydrogenation of polydienes.[79] The complete

hydrogenation of aliphatic polymers produced by ROMP yields perfectly linear polyethylenes. Perfectly linear, low polydispersity polyethylene has been recently synthesized in our group by the living polymerization of cyclobutene followed by hydrogenation.[80] It has also been synthesized by the polymerization and hydrogenation of polyocteneamer synthesized by ADMET polymerization.[81]. Also, a fluoroalkyl endcapped polyethylene was recently synthesized employing a ROMP/CT polymerization followed by hydrogenation.[82] Hydrogenation of a HTPBD produced by the above ROMP/CT scheme was investigated. For laboratory scale hydrogenations, the chemical hydrogenation procedure described by Hahn is convenient.[83] Following Hahn's procedure, the diimide reduction of a low-molecular-weight (<5.0 x 10^3) HTPBD was accomplished (eq 17).



(17)

In contrast to other HTPBD precursors synthesized by radical or anionic techniques, the HTPBDs synthesized by the ROMP/CT methodology are perfectly linear. The solubility of the HTPE shown in eq 17 is poor and the peak melting point was determined by DSC to be 133 °C. Both of these observations are consistent with a highly crystalline polyethylene. The ^{1}H NMR spectrum is shown in Figure 14. The methylene protons adjacent to the oxygen can be seen as the multiplet at 3.73. No olefinic protons are observed. Also an OH stretch at 3449 cm^{-1} was observed in the IR spectrum of the polymer. Assuming perfect difunctionality the $\overline{M_n}$ was calculated from the ^{1}H NMR spectrum to be 3400.

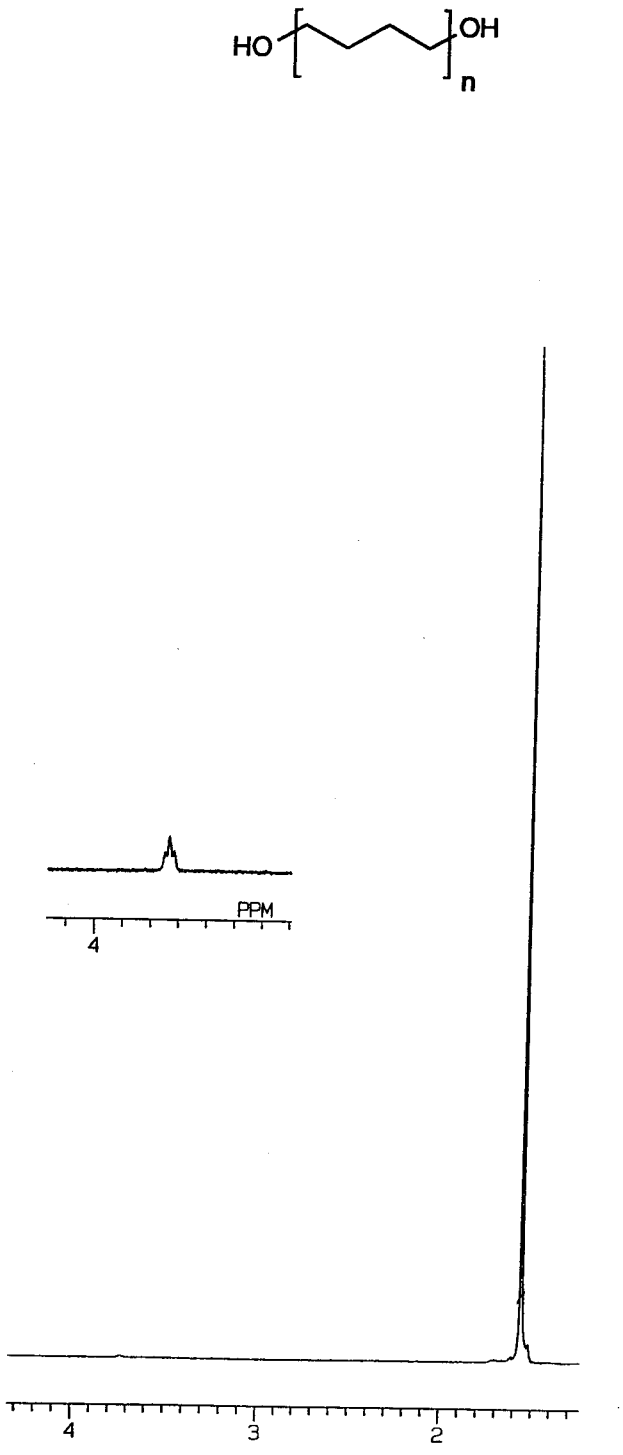


Figure 14. The ^1H NMR spectrum (400 MHz, chlorobenzene-d_5, 100 °C) of HTPE (scales are in ppm).

In preliminary experiments, this HTPE was used as a coating to prepare durable, non-pourous surfaces for applications such as water shedding surfaces. It was found that this HTPE when coated onto a polyurethane surface resulted in a significant lowering of the surface energy.[84]

Conclusions

The ROMP/CT method described above is a convenient method for the preparation of HTPBD. The repeat unit regiochemistry of the HTPBDs produced by this method was perfectly 1,4. Molecular weights of the HTPBDs can be controlled by the $[\mathbf{COD}]_o/[CTA]_o$ ratio. The structure of the endgroups is defined by the choice of the CTA. Generally, the number average functionalities for the HTPBDs were close to 2.0. Values less than 2.0 can be rationalized by the presence of large cyclic oligomers in the polymer sample or endgroups arising from the catalyst. Theoretically, the later contribution can be minimized if the ratio of CTA to catalyst is large. HTPBDs were synthesized in ROMP/CT systems employing catalysts **Mo**, **W**, and **Ru**. In comparison, the catalyst based on **Ru** is superior. Very high $[\mathbf{COD}]_o/[\mathbf{Ru}]_o$ ratios were employed in the synthesis of HTPBs using a CTA that can be made in one step from readily available starting materials.

Experimental Section

General Considerations. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4Å molecular sieves (Linde). NMR spectra were recorded on a JEOL GX-400 spectrometer (399.65 MHz 1H, 100.40 MHz 13C) or a GE QE-300 Plus (300.10 MHz ^{1}H; 75.49 MHz ^{13}C) spectrometer. Chemical shifts are reported in ppm (δ) downfield from tetramethylsilane and referenced to residual protio solvent. Coupling constants are reported in hertz (Hz). IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. Gas chromatographic analyses were performed on a HP-5890 Series II Gas Chromatograph with an SE-30 capillary column. GPC analyses in methylene chloride were obtained on a HPLC system utilizing an Altex Model 110A pump, a Rheodyne model 7125 injector with a 100 μL injection loop, through two American Polymer Standards 10 micron mixed bed columns, and a Knauer differential-refractometer. The molecular weights and polydispersities are reported versus monodisperse polystyrene standards. VPO was carried out using a Jupiter model 233 in toluene at 60 °C using sucrose octaacetate for calibration. The calibration was confirmed using a low-molecular-weight polybutadiene standard. GPC analyses in toluene were performed on a Waters model 150C at 60 °C. The molecular weights and polydispersities are reported versus monodisperse polystyrene standards. Elemental analysis was performed by Fenton Harvey at the California Institute of Technology Elemental Analysis Facility.

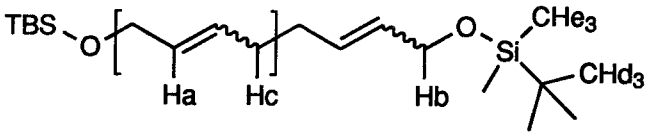
Materials. Toluene (Baker HPLC grade) was distilled from CaH_2 under argon and degasssed. Benzene (and C_6D_6) was distilled from Na/bezophenone

ketyl prior to use. 3-butyne-1-ol, butyl lithium, and TBAF were purchased from Aldrich and used without further purification. *cis*-2-butene-1,4-diol (**1**, Aldrich) was distilled from $CaSO_4$ under vacuum prior to use. Pivalaldehyde (Aldrich) was distilled from CaH_2 prior to use. **COD** (Aldrich) and filtered through neutral alumina before use. Ethylene oxide was purchased from Fluka, and TBSCl was purchased from Petrarch. All other solvents, salts, and other commodity chemicals were reagent grade and used without further purification. Complex **W** was graciously provide by Dr. Lynda K. Johnson. Initial quantaties of complex **Mo** were graciously provided by Dr. Greg C. Fu. Complex **Mo** was also synthesized in large scale according to the procedure by Schrock.[59]

Preparation of cis-TBSOCH$_2$CHCHCH$_2$OTBS (2). **1** (5.3 g, 60 mmol) was added to a DMF solution (150 mL) of imidazole (20.4 g, 300 mmol) and *tert*-butyldimethylsilylchloride (21.7 g, 144 mmol). The reaction mixture was heated to 40 °C and stirred for 17 h. The DMF solution was diluted with 200 mL of water and extracted with Et_2O. The organic layer was washed with water, dried over $MgSO_4$, and concentrated to give a nearly quantitative yield of the desired product. The clear oil was distilled twice from CaH_2 under reduced pressure (85 °C at 15 mmHg). ^{1}H NMR ($CDCl_3$): δ 5.53 (m, 2H), 4.21 (d, J=4Hz, 4H), 0.88 (s, 9H), 0.05 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 130.3, 59.7, 26.0, 18.4, -5.1; Anal. Calcd. for $C_{16}H_{36}O_2Si_2$: C, 60.69; H, 11.46. Found: C, 60.48; H, 11.77.

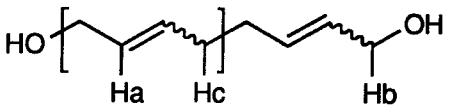
General Polymerization Procedure Employing COD, 2, and W. In a nitrogen filled glove box, **COD** (925 mg, 8.55 mmol) and **2** (50 mg, 0.16 mmol) were mixed in a glass vial. In a separate vial 10 mg of **W** was dissolved in 50

μL of dry, degassed benzene. The contents of the two vials were combined and the reaction mixture was stirred in the glove box for 2 h. After 2 h 50 μL of dry degassed pivalaldehyde was added to the vial. The polymerization mixture was allowed to stir for 18 h in the glove box. The mixture was dissolved in 3 mL of benzene, precipitated into 35 mL of methanol, and the polymer was isolated by centifugation. The resultant polymer was dried under vacuum overnight to yield 0.37 g of a light yellow oil (40%). GPC (CH_2Cl_2): $\overline{M_n}$ =14.1 x 10^3, PDI=3.0. The ^{1}H NMR spectrum was assigned as follows (δ):



^{1}H NMR (400MHz, CD_2Cl_2): δ 5.38 (bs, Ha cis), 5.43 (bs, Ha trans), 4.21 (d, Hb cis), 4.10 (d, Hb trans), 2.09 (bs, Hc cis), 2.02 (bs, Hc trans), 0.89 (s, Hd), 0.05 (s, He). Olefinic protons adjacent to the endgroup were not observed in the polymers isolated using this procedure and were presumably buried under the backbone olefinic protons.

General Deprotection of TBS Endcapped HTPBD. Deprotections were generally carried out in THF using a 5 fold excess of TBAF relative to TBS (as calculated from the intial amount of CTA added to the polymerization solution) at RT under argon. The polymer was precipitated in at least a 5 fold excess of methanol. Isolation of HTPBD was generally accomplished by centrifugation. Further purification of the light yellow oils was accomplished by filtration of a benzene solution of the HTPBD through neutral alumina. The ^{1}H NMR spectrum was assigned as follows:



^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.38 (bs, Ha cis), 5.43 (bs, Ha trans), 4.14 (m, Hb cis), 4.04 (m, Hb trans), 2.09 (bs, Hc cis), 2.02 (bs, Hc trans). Olefinic protons adjacent to the endgroup were not observed in the polymers isolated using this procedure and were presumably buried under the backbone olefinic protons.

Preparation of $HCCCH_2CH_2OTBS$ (4). 3-Butyne-1-ol (25 g, 357 mmol) was added dropwise to a stirred DMF solution (250 mL) of *tert*-butyldimethylsilylchloride (65 g, 431 mmol) and imidazole (61 g, 896 mmol) at 0 °C over 5 min. The solution was allowed to warm to RT over 15 min and heated to 40 °C for 45 min. The solution was removed from the heat and water (200 mL) was added. The resulting solution was extracted with hexane. The extracts were combined, washed with saturated LiCl, dried over $MgSO_4$, and concentrated to give 64 g (97%) of a clear oil. IR (neat): 3314, 1257, 1109, 838, 777; ^{1}H NMR ($CDCl_3$): δ 3.71 (t, J=7.2 Hz, 2H), 2.37 (m, 2H), 1.93 (t, J=2.7 Hz, 1H), 0.87 (s, 9H), 0.04 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 81.7, 69.3, 62.0, 26.0, 23.1, 18.4, -5.2.

Preparation of $HOCH_2CH_2CCCH_2CH_2OTBS$ (5). Anhydrous ammonia (500 mL) was condensed under argon at -40 °C into a 1 L 3-neck flask equipped with a dry ice/acetone condenser. Butyl lithium (96 mL, 2.5 M in hexane, 240 mmol) was added via syringe to the reaction flask at -40 °C, and the solution was stirred for 30 min. To this solution was added **4** (44 g, 239 mmol) via

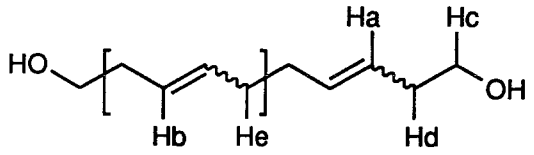
syringe. Ethylene oxide (15 mL, 300 mmol), which was precondensed at -78 °C, was then added via cannulla to the solution over 30 min. The reaction was stirred at -40 to -30 °C for 72 h with the dry ice/acetone condenser kept at -78 °C after which time the ammonia was allowed to evaporate. Water (200 mL) was added to the residue and then extracted with ether. The ether was concentrated and the yellow oil was distilled under reduced pressure (97-99 °C, 0.01 mmHg) to yield 21.2 g (39%) of a clear oil. IR (neat): 3354, 1256, 1105, 1050, 837; ^{1}H NMR ($CDCl_3$): δ 3.68 (m, 4H), 2.38 (m, 4H), 1.74 (bs, 1H), 0.88 (s, 9H). 0.05 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 79.5, 77.7, 62.1, 61.2, 26.8, 23.1, 18.3, -5.3. Only 8 peaks were observed in the ^{13}C NMR spectrum. The two propargyllic carbons are presumably overlapped. In **6** the two allylic carbons are only separated by 0.1 ppm.

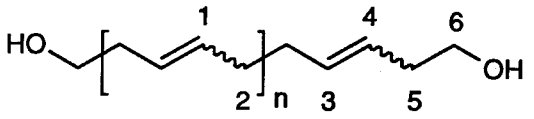
Preparation of cis-$HOCH_2CH_2CHCHCH_2CH_2OTBS$ (6). Following the procedure desribed by Brown,[56] **5** (10 g, 44 mmol, in 100 mL EtOH) was added to a solution of $Ni(OAc)_2{\cdot}4H_2O$ (11.5 g, 46 mmol), $NaBH_4$ (1.75 g, 46 mmol), and ethylene diamine (3.3 mL, 50 mmol) in EtOH (200 mL). H_2 was slowly bubbled through the solution until the reaction was complete by ^{1}H NMR spectroscopy (1-2 h). EtOAc:hexane (200 mL, 1:1 v/v) was added to the solution which was subsequently filtered through silica gel and concentrated. The resulting light green jelly was dissolved in EtOAc:hexane (200 mL, 1:1) and filtered through silica gel again to yield 8.7 g (86%) of a clear oil. IR (neat): 3333, 3011, 1256, 1097, 836; ^{1}H NMR ($CDCl_3$): δ 5.51 (m, 2H), 3.62 (m, 4H), 2.56 (m, 4H), 1.80 (bs, 1H), 0.87 (s, 9H), 0.03 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 129.4, 127.3, 62.8, 62.0, 30.9, 30.8, 25.9, 18.4, -5.4.

Preparation of cis-TBSOCH$_2$CH$_2$CHCHCH$_2$CH$_2$OTBS (7). **6** (2.25g, 9.8 mmol) was protected with TBSCl by the procedure described above for **4** to yield 3.37g (84%) of a clear oil. The oil was further purified by distillation from CaH_2 under reduced pressure (90-92 °C, 0.005 mmHg). GC 99.4 % pure, >95% cis; IR (neat): 3013, 2955, 2929, 2895, 1472, 1463, 1382, 1099, 937, 834, 737 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.44 (m, 2H), 3.58 (t, J=7 Hz, 4H), 2.25 (m, 4H), 0.87 (s, 9H), 0.03 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 127.6, 62.9, 31.3, 26.0, 18.4, -5.4; Anal. Calcd. for $C_{18}H_{40}O_2Si_2$: C, 62.72; H, 11.70. Found: C, 62.83; H, 11.32.

Large Scale Polymerization and Deprotection Procedure Employing COD, 7, and Mo. In a nitrogen filled glove box, **COD** (11.3 g, 104 mmol) and **7** (2.2 g, 6.4 mmol) were combined in a 100 mL Schlenk flask. 10 mL of dry, degassed toluene was added to the flask. To this solution a solution of **Mo** (33 mg, 0.043 mmol) in toluene (0.5 mL) was added. The resulting yellow solution became very hot and the toluene started to reflux. The solution slowly became viscous and turned orange. After 0.5 h the flask was removed from the glove box and 2 mL of degassed methanol was added to the flask and the solution was stirred for 10 min. 35 mL of a 1.0M TBAF in THF solution was added dropwise to the flask under argon. The resulting cloudy solution was stirred overnight at RT. The polymer was precipitated in methanol and it was determined by ^{1}H NMR that the polymer was not fully deprotected. The above deprotection sequence was repeated (optimization of the deprotection sequence was not investigated). The polymer was precipitated in methanol (200 mL) and was further purified by repeated precipitation of a THF solution of the polymer in methanol. The polymer was isolated and dried under vacuum at 45 °C overnight to yield 8 g (67%) of a clear, very light yellow oil

(the low yield in this case can be partially attributed to complications arising from the second deprotection step). $\overline{M_n}$ (VPO): 3250; $\overline{F_n}$ (VPO, ^{1}H NMR): 1.94; The ^{1}H NMR and ^{13}C NMR spectra[85] were assigned as follows:





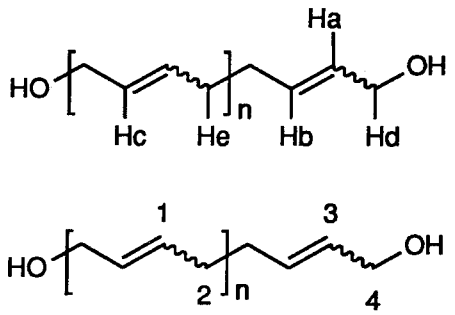
^{1}H NMR (500 MHz, $CDCl_3$): δ 5.5 (m, Ha cis and trans), 5.40 (m, Hb trans), 5.35 (m, Hb cis), 3.58 (m, Hc cis and trans), 2.25 (m, Hd cis and trans), 2.08 (m, He cis), 2.03; ^{13}C NMR (75MHz, $CDCl_3$): δ 134.10 (C4, tc), 134.01 (C4, tt), 133.14 (C4, cc), 133.11 (C4, ct), 130.50 (C1, tc), 130.37 (C1, tt), 129.98 (C1, cc), 129.81 (C1, ct), 126.64 (C3, tc), 126.52 (C3, tt), 125.92 (C3, cc), 125.71 (C3, ct), 62.65 (C6, t), 62.28 (C6, c), 36.35 (C5, t), 33.09 (C2, t), 31.25 (C5, c), 27.79 (C2, c).

Preparation of $AcOCH_2CHCHCH_2OAc$ (8). Acetic anhydride (reagent grade, 108g, 100ml, 2.5 eq) was added dropwise to a stirring methylene chloride/chloroform (~400ml, 1:1 v/v) solution of **1** (37.3g, 1 eq) and triethylamine (reagent grade, 107g, 148ml, 2.5 eq) at 0 °C over ~1 h. The solution was allowed to slowly warm up to room temperature and stirred overnight (or followed by TLC). The orange solution was washed with water (3 x 300 ml) and concentrated on a rotovap. The resultant orange oil was distilled under reduced pressure (~0.05 mmHg) and the middle fraction was collected at ~54 °C. The distillate was stirred over calcium hydride at room

temperature, overnight, under full vacuum (~0.05 mmHg). This was then redistilled under reduced pressure (as above ~54 °C) and collected in a Kontes flask which was sealed under argon. Isolated yield was ~58 g (80%). GC 100% pure, >97% cis. ^{1}H NMR ($CDCl_3$): δ 5.73 (m, 2H), 4.65 (d, J=5Hz, 4H), 2.05 (s, 6H). ^{1}H NMR (C_6D_6) cis: 5.50 (m), 4.48 (d), 1.62 (s), trans: 5.52 (m), 4.32 (d), 1.63 (s). ^{13}C NMR ($CDCl_3$): δ 170.2, 127.8, 59.6 (trans, 63.5), 20.5 (trans, 25.0). Anal. Calcd. for $C_8H_{12}O_4$: C, 55.81; H, 7.02. Found: C, 55.29; H, 7.08.

General Polymerization and Deprotection Procedure Employing COD, 8, and Ru. A three-neck, 250 mL, round bottom flask equipped with a mechanical stirrer, was charged with 1,5-cyclooctadiene (131 g, 1.22 mol, 4880 equiv). The chain transfer agent (**8**) (4.9 g, 0.0285 mol, 114 equiv.) was added to the reaction flask via pipet. The two open necks of the flask were capped with septa. The mixture was purged with a vigorous stream of argon through a needle (the outlet going to a oil bubbler) for 30 minutes. With a continual purge of argon, **Ru** (0.231g, 2.5 x 10-4 mol, 1 equiv.) was added as a methylene chloride solution (~1.2 mL) via syringe (**Ru** is very soluble in the **COD/8** mixture and can be added as solid). The reaction was kept under a slow purge of argon, the mechanical stirrer was started, and the flask was immersed in an oil bath at 45-50 °C. The dark red-orange reaction mixture was stirred for 6h. The resulting light orange reaction mixture was allowed to cool to room temperature and was poured into ~500 mL of slightly acidic methanol (add 15 mL of 1M HCl to 500 mL of methanol). The polymer that precipitates became white, and the methanol solution turned yellow. The methanol was decanted, and the methanol wash was repeated three times. The polymer was then dissolved in ~600 mL of tetrahydrofuran and cooled to 0 °C. 100 mL of

0.7 M sodium methoxide in methanol was added to the THF solution (a slight volume of THF was added because the polymer started to precipitate). This was stirred for 5.5h at 0 °C. The reaction mixture was poured into 1 L of slightly acidic methanol and stirred overnight at room temperature. The mixture was decanted and the polymer was washed three times with methanol/HCl, methanol/water, and pure methanol succesively. Care must be taken in these purification steps since very-low-molecular-weight telechelics are slightly soluble in THF/methanol mixtures. After the final wash the polymer was dissolved in 1 L of methylene chloride (reagent grade) and isolated by rotary evaporation and subjected to high vacuum at ~40 °C overnight to yield ~120g (~88%) of a clear, viscous liquid. IR (neat): 3320, 2914, 1655, 1435, 1352, 1312, 1081, 965, 726 cm^{-1}. The ^{1}H NMR and ^{13}C NMR spectra were assigned as follows:



^{1}H NMR (400MHz, $CDCl_3$): δ 5.6-5.7 (m, Ha and Hb, cis and trans), 5.40 (bs, Hc trans), 5.35 (bs, Hc cis), 4.16 (d, J=7 Hz, Hd cis), 4.06 (d, J=5 Hz, Hd trans), 2.06 (bs, He cis), 2.01 (bs, He trans); ^{13}C NMR (100MHz, $CDCl_3$): δ 132.8 (C3, tc), 130.5 (C3, tt), 130.2 (C1, tc), 130.1 (C1, tt), 129.7 (C1, cc), 129.5 (C1, ct), 63.8 (C4, t), 58.6 (C4, c), 32.8 (C2, t), 27.5 (C2, c).

Hydrogenation of HTPBD. A low-molecular-weight (13g, $\overline{M_n} \approx 2.0 \times 10^3$, [olefin]=0.24 mmol) HTPBD synthesized by a ROMP/CT polymerization using **8** as the CTA and **Ru** as the catalyst was dissolved in 500 mL of *o*-xylene and 100 mL of tri-*n*-butyl amine. 90g of *p*-toluenesulfonhydrazide (0.48 mmol) were added to the solution. The reaction mixture was heated to reflux for 17 h. The red/orange mixture was allowed to cool and precipitated with acetone. The polymer was washed several times with acetone or ethanol and isolated by centrifugation. The snow-white polymer was isolated in high yield. Mp (DSC): 133 °C; IR (KBr pellet): 3449, 2919, 2815, 1630, 1473, 718 cm^{-1}; ^1H NMR (chlorobenzene-d_5, 100 °C): δ 3.73 (bt, 4H), 1.16 (s, 481H). The molecular weight of the polymer calculated by ^1H NMR assuming a functionality of 2.0 was ~3400.

Appendix I

Recommended procedure for the preparation of HTPBD from the ROMP of COD by Ru in the presence of 8.

(See Experimental Section for a detailed description)

1) Calculate the desired $\overline{X_n}$ (COD repeat unit = 108.18) and use this as the mol ratio of **COD** to **8**. Calculate the amount of **Ru** necessary to keep $[\mathbf{8}]_o/[\mathbf{Ru}]_o \geq 200$.

2) Filter the unpurified **COD** through activated neutral alumina (to remove inhibitor and other polar impurities) into a round-bottom flask equipped with a stir bar or mechanical stirrer.

3) Add prepurified (distilled from CaH_2) **8** to the round-bottom flask.

4) Purge the mixture with a steady flow of anhydrous, oxygen-free argon for 30 minutes.

5) Add **Ru** as a solid and purge with argon for an additional 10 minutes.

6) Cap the round-bottom flask with a septum and keep a slow purge of argon over the reaction mixture.

7) Heat the flask to ~50 °C for 24 h (rate will depend on amount of catalyst used and the progress can be followed by ^1H NMR spectroscopy) and stir.

8) Pour the reaction mixture into 2-5 times the volume of slightly acidic methanol (15 mL of 1M HCl in 500 mL of methanol). Repeat the methanol wash until the polymer is colorless.

9) Dissolve the polymer in a minimum amount of THF. Cool to 0 °C and add enough 0.7M sodium methoxide in methanol so the ratio of $[\mathbf{8}]_o/[\text{NaOMe}] \approx$

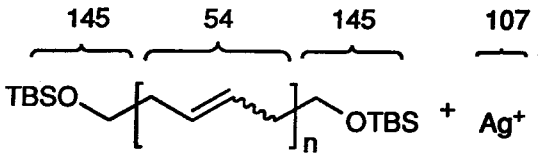
0.4 (e.g. for 5 g of 8 use 100 mL of 0.7M NaOMe in methanol). Add more THF if the polymer starts to precipitate. Stir at 0 °C for 6 h.

10) Repeat the precipitation procedure used in step 8. Wash with both acidic methanol, a methanol/water mixture, and pure methanol.

11) Isolate polymer and dry under vacuum at 30-45 °C for 12 h.

Appendix II

A low-molecular-weight, TBS protected HTPBD synthesized using **Mo, 7** and **COD** was analyzed by time-of-flight secondary ion mass spectrometry (TOF-SIMS).[86-88] The polymer was desorbed from a silver substrate, and silver is also desorbed to stabilize and cationize the polymer. The mass spectrum is shown in Figure 16. Each peak corresponds to an intact polymer with exactly two endgroups. No other species were observed. From the ^1H NMR spectrum, assuming perfect difunctionality, the $\overline{M_n}$ was calculated to be 1780. From the TOF-SIMS spectra a $\overline{M_n}$ of 734 was calculated. For polystyrene, TOF-SIMS $\overline{M_n}$ values are quite accurate. From this preliminary analysis it would seem that this is not the case for HTPBD. The analysis was performed by Anna Belu in collaboration with professors R. Linton and J. DeSimone at the University of North Carolina.



Peaks correspond to exact mass intact oligomers

mass = 54n + (2 x 145) + 107

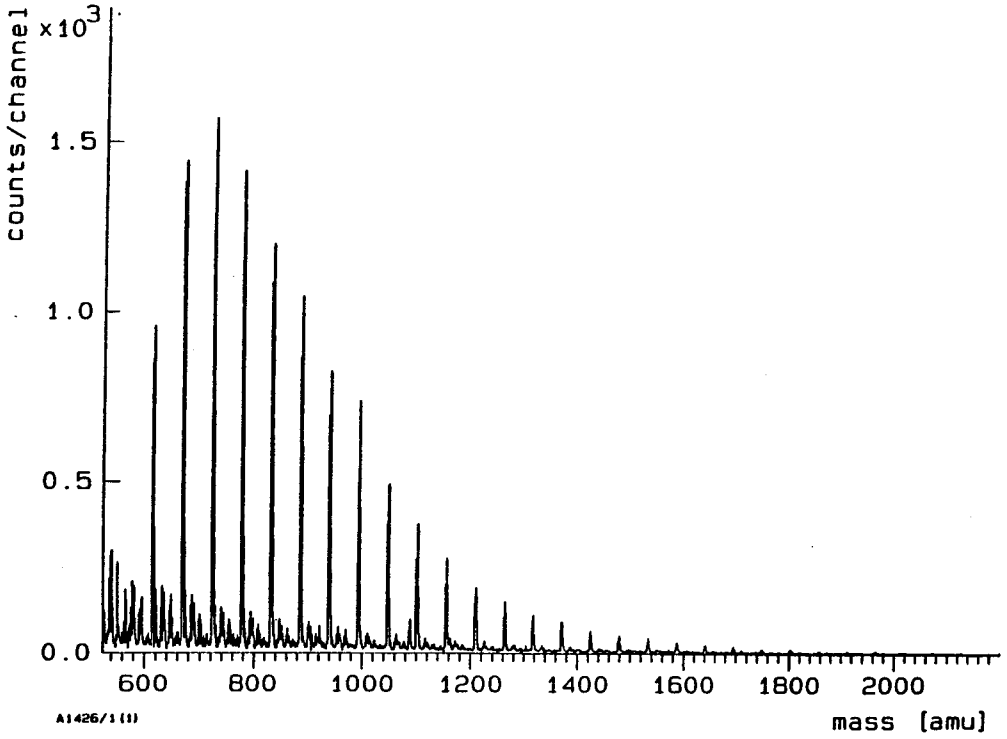


Figure 15. TOF-SIMS spectrum of a low-molecular-weight, TBS protected HTPBD.

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